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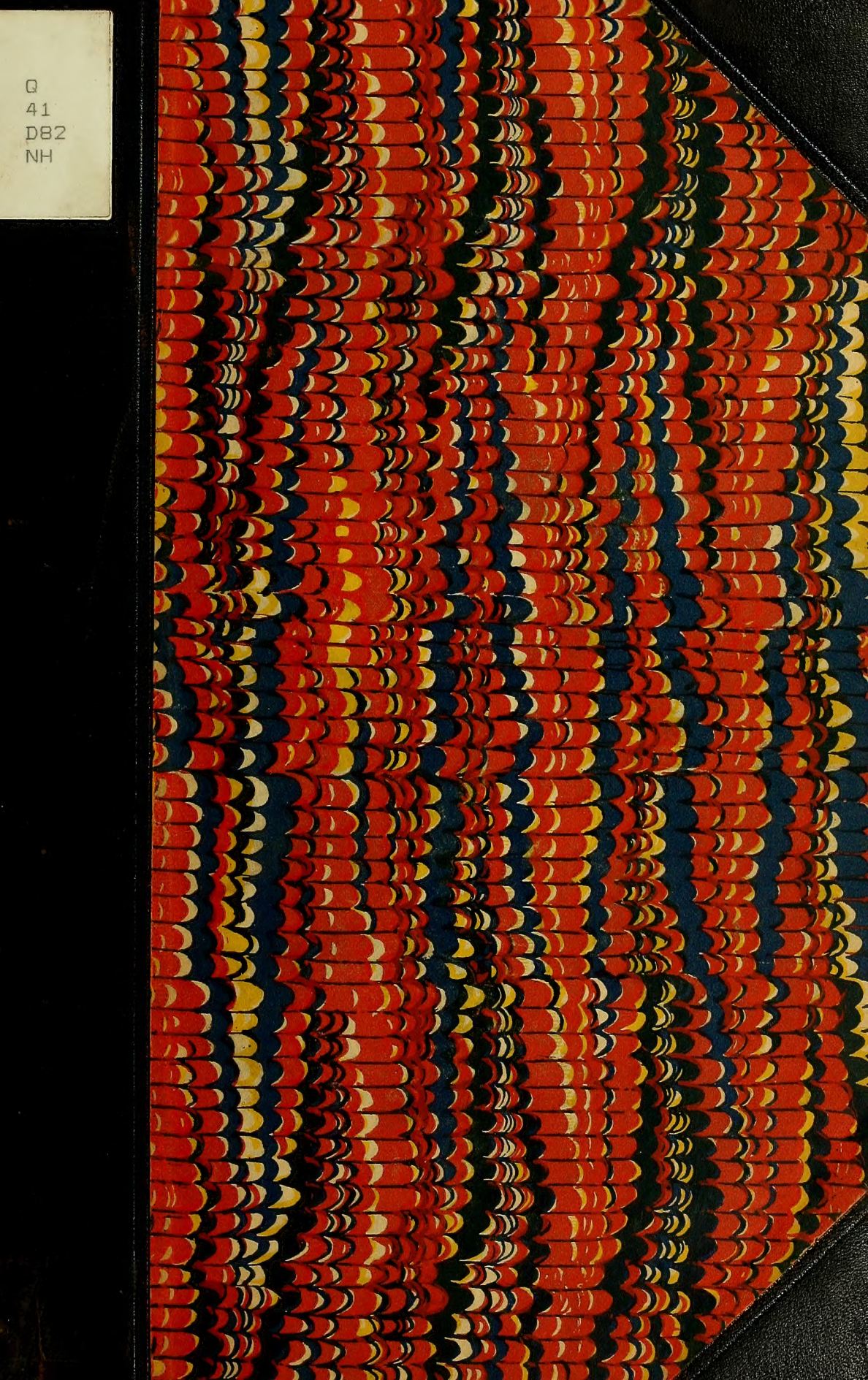

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THE

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ERRATUM

p. 63, line 2, *for* "oxygen" *read* "water."

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Vol. XVI. (N.S.), No. 1. JANUARY, 1920.

A CRYOSCOPIC METHOD FOR THE ESTIMATION OF SUCROSE.

Smithsonian Institution
MAR 5 1921
National Museum

BY

HENRY H. DIXON, Sc.D., F.R.S.,

UNIVERSITY PROFESSOR OF BOTANY IN TRINITY COLLEGE, DUBLIN;

AND

T. G. MASON, M.A., Sc.B.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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THE

SCIENTIFIC PROCEEDINGS

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THE ROYAL DUBLIN SOCIETY.

I.

A CRYOSCOPIC METHOD FOR THE ESTIMATION OF SUCROSE.

By HENRY H. DIXON, Sc.D., F.R.S.,

University Professor of Botany in Trinity College, Dublin;

AND

T. G. MASON, M.A., Sc.B.[1]

Read December 16, 1919. Published January 9, 1920.

The depression of freezing-point caused by a given quantity of sucrose in a given volume of water is approximately doubled after inversion. It is evident, therefore, that by two cryoscopic observations—before and after inversion—the sucrose-content of a solution can be determined. By using the Thermo-electric Method of Cryoscopy (2) the estimation can be effected on small amounts of fluids, and, as the presence of colloids introduces no difficulties, it should furnish a rapid and sufficiently accurate means of estimating the sucrose-content of physiological fluids.

The following investigation was undertaken to work out the details of the method, and to test its applicability to plant saps.

---

[1] Mr. Mason was enabled by a maintenance grant from the Department of Research to engage in this research.

Apparatus.

The construction of the thermo-couples employed, and the general arrangements of the thermo-electric method, have already been described (2), and it is unnecessary to go into them here. Slight modifications have, however, been introduced. Instead of single drawn pine rods to support the wires of the couple, double ones, slightly flattened on the surfaces of contact, were employed. This gives greater strength, and affords a means of protecting the eureka and copper wires forming the couple, which run down the grooves on each side of the double pine supports. One of the pieces of pine is cut away close to the lower end of the support, thus forming a recess in which the junction is freely exposed to the surrounding fluid. Collodion varnish was used to waterproof the insulated wires, and to cement the pine rods together, and to keep the wires in position. In case it is desired to alter the sensitiveness of the couple, or modify the couple in any way, it is easy to dissolve off the collodion with acetone, and substitute a new eureka wire of different resistance.

Calibration of the Thermo-couples.

Sucrose was employed as a standard for the calibration of the thermo-couples. It was selected for this purpose, not only because it can be readily obtained of great purity, but its depressions of freezing-point, which are known with great precision from Raoult's researches, can be more easily determined than those of other substances, whose solutions are not hydrated to the same degree. The ease with which it undergoes inversion on storage is, however, a serious disadvantage to its use; and as it is not always possible to make up standard solutions for every calibration, calcium chloride solutions of suitable concentration, whose freezing-points had been determined against sucrose, were used for this purpose.

The importance of frequently calibrating the instrument has already been emphasized (2).

Thermo-couples producing deflections of from two to three hundred millimetres per 1° C. have been constructed with a single pair of junctions, the degree of sensitiveness varying with the resistance of the eureka wire employed. The calibration of a thermo-couple producing a deflection of 294·5 mm. per 1° C. is shown in Table I. In this approximately 30 cm. of eureka wire, 0·100 mm. diam., and two leads each of copper wire, 0·200 mm. diam., were used. In the last column of the Table are given the actual freezing-points of the solutions derived from Raoult's results quoted by Hamburger (4).

Table I.

Gm. of Sucrose per 100 gm. of Water.	Deflection Obs. I.	Deflection Obs. II.	Deflection Obs. III.	Deflection Mean.	Freezing-point from Raoult.
1	15·75	15·88	15·75	15·8	0·054°
2	32·5	32·0	31·5	32·0	0·108°
3	47·13	48·0	47·38	47·5	0·163°
4	63·25	63·0	63·5	63·3	0·218°
5	80·25	80·0	80·75	80·1	0·272°
6	95·5	95·75	95·25	95·5	0·328°
7	113·25	112·75	113·5	113·1	0·383°

It will be observed that a thermo-couple as sensitive as that used in this calibration can only register depressions of freezing-point up to 0·849° (294·5 mm. = 1°). This limitation, of course, is imposed by the scale. Where the solution to be examined has a greater depression than this, it is necessary to substitute for distilled water a standard freezing below 0°. Solutions of calcium chloride, whose depressions have been previously determined, can be employed. Though this solution may be used in place of distilled water in these cases, it is not as easy of manipulation as a pure liquid, where ice may continue to separate without alteration in freezing-point. On the whole, it has been found more satisfactory, where a greater range is desired, to construct a less sensitive thermo-couple, and to keep distilled water as the standard.

Estimation of Sucrose in made-up Solutions.

To effect the inversion of sucrose, small quantities of invertase prepared by Davis' method (1) were used. It is undesirable to dilute unnecessarily the solution, so only that quantity of invertase is added which will ensure inversion. Allowance must subsequently be made for the dilution of the solution with the water added in the invertase, and also for the depression of freezing-point produced by the solutes in the invertase solution and the toluene added with it. The invertase solution employed had a moisture-content of 83 per cent.

In each of the observations two test tubes of about 10 c.c. capacity were used. Into one approximately 5 gm. of the sucrose solution (2 gm. of sucrose

per 100 gm. of water) was weighed, and into the control tube a similar amount of distilled water. From a previously calibrated capillary tube 0·32 gm. of invertase solution was introduced into each test tube. (In Obs. 2 only 0·24 gm. was used), and then a drop of toluene on a glass rod, with which the mixtures were briskly stirred.

The test tubes were then tightly corked and stored at 28° in a thermostat; on withdrawal of the first six on the following day (approximately 24 hrs.) the deflections produced by the freezing-point depressions of the sucrose-invertase solutions and the controls (invertase solutions) were independently determined against distilled water. The solutions used in the subsequent five observations were left in the thermostat for another day, and then examined in a similar way.

It is more direct, and has been found more satisfactory, to add a measured quantity of the invertase-toluene mixture to the weighed sucrose solution, keeping both at a low temperature to prevent premature inversion. Then, without allowing the temperature to rise, a determination of the freezing-point is made. The second freezing-point determination is made after incubation, and the difference of the two depressions found is a measure of the sucrose inverted.

For example, in Obs. 1, Table II, the deflection produced by the solution before the addition of the invertase was 33 mm., so that 31·0 (viz. 64·0—the corrected deflection for the sugar-invertase mixture—less 33), represents the increase in deflection due to inversion; 304·1 mm. with this thermo-couple represents 1°. Hence, the increase representing a difference in depression of freezing-point of only 0·101° (0·210° – 0·109°), it is evident that the inversion was not complete. Complete inversion of the sucrose present would have produced an increase in the depression of freezing-point of 0·108°. This stage has been reached, and is recorded in the observations made after 48 hours. The results afford an index as to the agreement that may be expected when sucrose is inverted under these conditions.

As the invertase solution employed had a needlessly low depression of freezing-point, and was not of great activity, being prepared two years previously, a new preparation was made, which was used in subsequent observations.

In Table III are shown the results obtained on inverting a sucrose solution containing 4 gm. of sucrose in 100 gm. of water under the conditions described in the last experiment. The weight of invertase solution employed was approximately 0·38 gm. per 5 gm. sucrose solution. That inversion was complete in this experiment is evident from the figures presented in the last column

TABLE II.

2 gms. Sucrose per 100 gms. H_2O. ($\Delta = 0{\cdot}109°$.)

DEFLECTION OF THERMO-COUPLE, 304·1 mm. per 1° C.

Time in Hours.	No. of Observation.	No. of Gm. of Sugar Solution.	Deflection of Sugar + Invertase Solution.	Deflection of Control.	Δ of Sugar Solution after Inversion.
24 hours	1	5·07	103·3	42·5	0·210°
	2	5·07	102·6	39·4	0·216°
	3	5·00	100·1	39·4	0·210°
	4	5·02	96·7	37·0	0·207°
	5	5·01	100·8	40·5	0·209°
	6	5·02	101·1	45·1	0·194°
48 hours	7	5·00	106·1	41·9	0·222°
	8	5·00	106·9	42·0	0·225°
	9	5·03	107·5	41·6	0·228°
	10	5·02	100·8	39·9	0·211°
	11	5·02	94·6	30·6	0·222°

TABLE III.

4 gm. Sucrose per 100 gm. Water diluted by addition of Invertase Solution to 3·75 gm. of Sucrose per 100 gm. of Water ($\Delta = 0{\cdot}204°$, Raoult).

DEFLECTION OF THERMO-COUPLE, 302 mm. per 1°.

No. of Sample.	Deflection for Sugar and Invertase Sol. after Inversion.	Deflection for Control.	Δ of Sugar Sol. after Inversion.
1	166·1	39·5	0·419°
2	164·7	41·0	0·410°
3	165·1	39·6	0·415°
4	162·7	36·8	0·417°

Method applied to the Estimation of the Sucrose content of Saps.

It has been demonstrated by Dixon and Atkins (4) that the application of intense cold renders tissues permeable, and so provides a means of extracting by pressure a representative sample of the sap. In their work liquid air was employed; as this, however, was not available, a freezing mixture of salt and ice has been employed. That the temperature thus obtained is capable of rendering the tissues permeable is shown elsewhere.

An experiment carried out on the leaves of *Galanthus spicatus* will illustrate the method adopted for determining the sucrose-content, and will give some idea of the accuracy that may be expected of it.

The leaves were gathered at 9.30 a.m., April 26th, from two clumps of this plant growing side by side. From one clump light had been excluded for five days. The leaves were then packed in large test tubes, which, after corking and sealing with plasticine, were submerged in the freezing mixture [– 16°] for two hours. On removal of the corks the tissues were found to be frozen solid; they were not, however, taken from the test tubes till they were somewhat thawed. On withdrawal of the material it was wrapped in linen, and pressed in a vice between two silver discs; about 30 c.c. were collected from each sample. In order to check the immediate activity of the enzymes, the sap was collected in test tubes and jacketed in ice.

Fifteen cubic centimetres of each sample were then boiled to kill the enzymes in half-inch test tubes, fitted with reflux condensers, by immersion for one minute in a brine bath. The freezing-points of the sap before and after this treatment are shown in Table IV; a slight lowering of the depression took place in both samples.

TABLE IV.

Description of Sample.	Δ of sap before boiling and filtering.	Δ of sap after boiling and filtering.
Sap pressed from exposed leaves, . . .	0·755°	0·748°
Sap pressed from leaves covered for five days,	0·703°	0·698°

Two test tubes (about 10 c.c. capacity), each containing 5 gm. of the boiled and filtered sap of each sample, were then immersed in a freezing bath [– 2°].

As soon as the saps had taken up the temperature of the bath, 0·33 gm. of invertase solution was added from a capillary tube. The sap-invertase solutions were then inoculated with a little hoar frost and their freezing-points determined. After storage overnight at 28°, the depressions were again observed. That inversion was complete was ascertained by raising to boiling-point as before, and again determining the freezing-points. In Table V are shown the depressions of the sap-invertase solutions before and after inversion. The difference in the observed depressions have been corrected for the dilution due to the addition of the invertase solution; in the final column are shown the equivalent concentrations of sucrose.[1] It will be observed that no correction has to be made for the solutes introduced with the invertase solution. It is of great importance that the saps should be cooled below 0° before the addition of the invertase, or otherwise immediate inversion will take place, and the results obtained will be too low.

TABLE V.

DEFLECTION OF THERMO-COUPLE, 161·7 mm. per 1°.

Description of Sample.	Moisture per cent.	No. of Expt.	Δ_1 Before Inversion.	Δ_2 After Inversion.	$\Delta_2-\Delta_1$.	$\Delta_2-\Delta_1$ Corrected for Dilution by Invertase.	Gm. Sucrose per 100 Gm. Sap.
Sap pressed from leaves: covered for five days.	93·55	i	0·762°	0·805°	0·043°	0·045°	0·83
		ii	0·763°	0·802°	0·039°	0·041°	0·76
Sap pressed from exposed leaves.	94·19	iii	0·809°	0·860°	0·051°	0·054°	1·00
		iv	0·812°	0·866°	0·054°	0·057°	1·06

A consideration of importance in favour of the cryoscopic method is the absence of any preliminary treatment for the purpose of clearing the sap of gums, etc.; this treatment is, of course, necessary before polarimetric or copper methods can be employed.

It is, however, for work in relation to the osmotic pressure in plants that the method has been elaborated, and is especially applicable.

An approximate comparison of the delicacy of the cryoscopic method

[1] The values here assigned to the increase in depression are based on the assumption that the freezing-point depression of sucrose is exactly doubled on inversion; this is not true to the thousandth of a degree.

with the volumetric method with Fehling solution may be made as follows :— As usually made up, 100 c.c. of Fehling solution is decolourized by 0·5 gm. dextrose, or slightly less sucrose. Reading to 0·2 c.c., the probable error is 0·001 gm.

With the cryoscopic method, readings of temperature may be obtained with an error of ± 0·003°; 0·01° corresponds to 0·2 per cent. of sucrose. Only 2·5 c.c. is necessary for the determination, so that the probable error is 0·0016 gm.

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Vol. XVI. (N.S.), No. 2. JANUARY, 1920.

THE CARBONIFEROUS COAST-SECTION AT MALAHIDE, CO. DUBLIN.

BY

LOUIS B. SMYTH, B.A., Sc.B.,

LECTURER IN PALÆONTOLOGY, UNIVERSITY OF DUBLIN.

[Authors alone are responsible for all opinions expressed in their Communications.]

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MAR 5 1921

II.

THE CARBONIFEROUS COAST-SECTION AT MALAHIDE, CO. DUBLIN.

By LOUIS B. SMYTH, B.A., Sc.B.,

Lecturer in Palæontology, University of Dublin.

Plates I and II.

Read November 25, 1919. Published February 11, 1920.

I.—Description of Section.[1]

The section lies about nine miles N.E. of Dublin and one mile E. of Malahide, and is a little over one mile in length. It consists of limestones and shales, the former being in places dolomitized. The rocks are exposed almost exclusively between tides. The general dip is northwards. The more argillaceous beds show cleavage dipping at 60° towards N., 35° W.

Three faults interrupt the sequence. Of these, the southern occurs just under the Carrickhill martello tower, and will be referred to as the Carrickhill fault. The middle one is 120 yards S. of the coastguard station, and will be called the C.G. fault. The northern (N. fault) is 230 yards N. of the coastguard station, and is marked by a dyke-like mass of dolomite.

The exposure is thus divided up by the three faults into four blocks, which are lettered in the accompanying map E, F, G, H, respectively, from N. to. S.

The commonest type of rock is a very impure, shaly limestone, full of lenticular masses of purer limestone, mostly of small size. These lenticles have frequently had their original orientation altered by the pressure which produced the cleavage. In such cases the bedding is only to be made out when viewed from a distance, or when layers of shells are present.

Parts of the exposure are much dolomitized, sometimes sufficiently to completely destroy the fossils. This is particularly the case in the vicinity of the northern fault.

Thick beds of shale are found at the extreme northern end, and also south of the Carrickhill fault. As will be seen in the sequel, the latter beds belong to a horizon a little higher than the former. Elsewhere thin beds of shale occur occasionally.

[1] Reference : Geol. Survey, Ireland, 1-inch map, sheet 102.

At the northern end the beds disappear under the sand of the Malahide inlet. The next exposure in this direction occurs at a distance of one and a quarter mile, at Portraine, and consists of Bala rocks.

To the south the rocks are covered by the Velvet Strand of Portmarnock, the next considerable exposure being the Lower Carboniferous of Howth, three miles away. There is, however, in certain states of the sand, a reef of nodular limestone uncovered 250 yards S. of the continuous exposure.

At Carrickhill the actual fault is concealed by sand. The strike of the fault is about N. 30° W. On the N.E. side the beds have a dip to the N.W., except in close proximity to the fault, where they bend round rather sharply and dip towards the fault, making it almost certain that this is the up-throw side.

S.W. of the fault the beds are greatly disturbed, the shaly beds being twisted into zig-zags, the limestones squeezed into lenticles, or fractured, and full of calcite veins. A series of parallel displacements of slight throw, having nearly the same strike as the fault, occur at intervals down to the S. end of the section. These all have the down-throw to the S.W.,[1] which supports the view that this is the direction of throw in the main fault. The amount of stratigraphical throw is estimated at over 780 feet (see p. 17).

The C.G. fault strikes E. and W., and is seen in the cliff to hade to the S. The beds immediately to the N. of it are dolomitized, and form a gentle anticline, thus dipping towards the fault. Immediately S. of the fault the beds are shattered, and full of calcite veins. There is also some dolomitization for a few feet. In places the beds on this side can be seen to be sharply upturned in contact with the fault. The indications are, therefore, that it is a normal fault, with the down-throw to the southward. The amount of stratigraphical throw is estimated at 330 feet (see also p. 15).

The northern fault is rather obscure. It is occupied by a thick vein of dolomite, and the rock is brecciated in its immediate neighbourhood. The beds on either side dip away from it at 35°, and are strongly dolomitized for about 30 yards, all fossils being obliterated. There is nothing to indicate the direction of hade. The amount of throw must be small, as the fauna on the two sides is almost identical. This being so, the down-throw must be to the north, as otherwise there would be a repetition of beds, which is not the case.

In the Geological Survey 1-inch map, sheet 102, and memoir to sheets 102 and 112, *only one fault* is recognized, namely, that at Carrickhill tower,

[1] A thick band of light grey limestone occurs under the martello tower. This is repeated twice (as indicated on the map, Pl. II) by the smaller faults, and immediately shows the amount and direction of displacement.

and it is taken to have the *down-throw to the N.* To quote the memoir referring to the beds S. of this fault :—

"These are precisely similar in lithological character to beds which are frequently found at the base of the limestone in the S. of Ireland (and also in S. Wales), and are called therefore the Lower Limestone Shales. . . . Just on the S. side of the martello tower here there is a sudden twist in the beds, beyond which there is an equally sudden change in their lithological character. It is supposed, therefore, that a fault traverses the limestone here, having *probably* a down-throw to the N., and being *perhaps connected in some way* with the one just described as to be observed in the railway, *where, however, the throw is in the opposite direction.*"[1] (The italics are mine.)

The amount of down-throw[2] to the south of this railway fault is estimated on p. 56 of the memoir as greater than 750 feet—a figure curiously close to my estimate for the Carrickhill fault (see below, p. 17.).

With regard to the other two faults, the C.G. fault can, as before mentioned, be seen in the cliff. It was, however, impossible to tell whether it was a dislocation of any importance, until the corresponding fossiliferous bands were discovered on either side. But it is curious that this fault is not even mentioned in the memoir.[3]

I did not myself recognize the northern fault as such during my first visit. It seemed to be simply an anticline somewhat "stretched" at the crest. Only by noting down in detail the beds and their fossil contents in either limb of this "anticline" did it become clear that correlation was impossible.

II.—FAUNA[4] AND CORRELATION.

Block E, upper part (M 1, 2, 3, 4*a*, *b*, *c*).[5] 290 feet = C_1.

Abundant—

Zaphrentis densa, Carruthers.
Syringopora θ, Vau.
Athyris cf. *glabristria*, Phill.
Syringothyris laminosa, McCoy.
Conocardium fusiforme, McCoy.

[1] P. 56. [2] The context shows that this is "stratigraphical" throw.

[3] By the courtesy of the officers of the Geological Survey of Ireland, I was able to consult the MS. 6-inch map, from which the 1-inch was reduced. I there find three parallel lines drawn E. and W., one at this fault, the other two close to it to the S.

[4] Only corals and brachiopods are recorded, except in the case of a few molluscs which happen to be abundant.

[5] These symbols refer to groups of beds as indicated on the map.

Less common—

Zaphrentis omaliusi, Ed. & H., Carruthers.
„ *delanouei*, Ed. & H., and *parallela*, Carruthers
Endophyllum irregulare, sp. nov.
Caninia cylindrica, Mut. Z or γ.
Amplexus coralloides, Sow.
Michelinia aff. *megastoma*, Phill.
Productus burlingtonensis, Hall. Rare.
Pustula tenuipustulosa, I. Thomas.
Schelwienella crenistria, Phill.[1]
Leptaena analoga, Phill.
Rhipidomella Michelini, L'Ev.
Spirifer aff. *clathratus*, McCoy, Vau.
„ sp. (striate. ? *attenuatus*).
Spiriferina octoplicata, Mut. δ, Vau.
Syringothyris texta, Hall. ?
Reticularia aff. *lineata*, Mart.

This is the fauna referred to by Vaughan at page 16 of his "Belgian paper"[2] as agreeing closely with the Petit Granit of the Écaussines area. It is therefore of C_1 age.

The dip is slight, and a considerable area of each bed is exposed. The surface of many of the lower layers is covered with large colonies of *Syringopora*, weathered out in dome-shaped masses, very much as they must have appeared on the ancient sea-bottom. In very many cases the clumps can be seen to be attached to enormous valves of *Conocardium fusiforme*, McCoy (as noted on the Survey Map). Shells may be found covered with the *Aulopora*-like bases of colonies.

The following points are noteworthy :—

Chonetes is entirely absent.

Caninia cylindrica is small and poorly developed, but appears to be at the Mut. Z or Mut. γ stage.

Schelwienella crenistria has not the Mut. C type of ribbing.

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[1] Poorly preserved. Convex brachial valve. Strong growth halts. Alternation of ribbing rarely marked. Cardinal angles not seen.

[2] Q. J. G. S., vol. lxxi, 1915.

Zaphrentis delanouei occurs as high up as M 3. It is small, but a section immediately below the floor of the calyx (diam. 6·5 mm.) has the typical shape of fossula.

Block E, lower part (M 4*d* & M 5). 180 feet = Z_3.

Abundant—

Michelinia aff. *megastoma*, Phill.
Cyathaxonia cornu, Mich.
Zaphrentis densa, Carruthers.
„ *delanouei*, Ed. & H., Carruthers.
Seminula, cf. *ambigua*, Sow. (in one bed).
Camarotoechia aff. *Mitcheldeanensis*, Vau.

Less common—

Amplexus coralloides, Sow.
Syringopora θ, Vau.
Productus burlingtonensis, Hall.
Pustula subpustulosa, I. Thomas. ?
Schelwienella crenistria, Mut. Z, Vau.
Spirifer aff. *clathratus*, M'Coy, Vau.
Syringothyris laminosa, M'Coy.
„ sp. (cuspidate).
Athyris glabristria, Phill.
Dielasma sp.

At M 4*d* the fauna changes markedly. That below no longer contains vesicular *Caninia*, and *Zaph. delanouei* becomes common. I have therefore assigned these beds to Z. The presence here of a small form of *Michelinia megastoma* would fit in with this correlation.

Camarotoechia aff. *Mitcheldeanensis* forms a marked element in the fauna from M 4*d* to the base of the Malahide exposure.

Seminula, cf. *ambigua*, has only been found here, and appears to be confined to one bed. If the correlation is correct, this is the lowest record of this genus of which I am aware.

No attempt has been made to correlate any of the Malahide beds with horizon γ. The latter is defined as the band of overlap of two faunal assemblages in the S. W. P. It ceases to have a meaning where the assemblages and conditions differ considerably from those in the S. W. P.

Block F (M 6, 7, 8, 9). 310 feet = Z. (M 7 is a repetition of M 6.)

Abundant—

Syringopora θ, Vau. (on *Euomphalus*). (M 6, 7.)
Productus burlingtonensis, Hall. (M 6, 7, 8, 9.)
Schelwienella crenistria, Mut. Z. Vau. (M 6, 7.)
Syringothyris carteri, Hall. (M 8.)
Athyris glabristria, Phill. (M 8, 9.)
Camarotoechia mitcheldeanensis, Vau. (M 9.)
„ aff. *mitcheldeanensis*, Vau. (M 7.)

Less common—

Amplexus coralloides, Sow.
Zaphrentis omaliusi, Ed. & H., Carruthers.
„ *densa*, Carruthers.
„ *delanouei*, Ed. & H., Carruthers.
Vaughania cleistoporoides, Garwood.
Productus (*Avonia*), cf. *youngianus*, Dav.
„ „ sp. (? aff. *bassus*, Vau.).
Syringothyris laminosa, M'Coy.
Spiriferina aff. *octoplicata*, Sow. ? ?
Reticularia aff. *lineata*, Mart.
Orbiculoidea sp.

It seems best simply to correlate these beds with Z, without attempting to divide them. *Zaphrentis densa* is common at the base, which might suggest that we have only got Z_2. This, however, would be an unsafe inference in view of the fact that there are some unexpected phenomena at Malahide; for example, *Spirifer clathratus* is only abundant well up in C, and *Seminula* occurs below C.

Syringothyris carteri, Hall, which is extremely abundant in M 8, agrees in every way with Schuchert's description of the American shell,[1] even as regards the mode of preservation, which, he says, is usual, i.e. crushed in shale. The characteristic "twilled" ornament of Syringothyris is well seen in the Malahide material. This shell is reported from β of Burrington[2] and from β and Z of Belgium.[3]

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[1] Ninth Ann. Rep. State Geologist. New York, p. 30.

[2] Reynolds and Vaughan, Q. J. G. S., vol. lxvii, 1911 ("Burrington Paper"), p. 364 (*S. typa*, Winchell).

[3] Vaughan, Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), pp. 8–10.

Block G (M 10, 11, 12). 300 feet = Z. (Repetition of M 7, 8, 9.)

Abundant—

Syringopora θ, Vau. On *Euomphalus* in M 10.
On *Schelwienella* in M 12.
Zaphrentis delanouei, Ed. & H., and *parallela*, Carruthers.
Productus burlingtonensis, Hall.
„ (*Avonia*) sp. (? aff. *bassus*, Vau.).
Schelwienella crenistria, Mut. Z, Vau.
Syringothyris carteri, Hall.
Athyris glabristria, Phill.
Camarotoechia aff. *mitcheldeanensis*, Vau.

Less common—

Spirifer roëmerianus, de Kon.
Eumetria sp.

These beds are a repetition of M 7, 8, 9. Owing to the sameness of lithology throughout, this was not recognized until the fauna had been carefully collected. The following succession, from above downwards, was noted in each series :—

(*a*) *Syringopora* growing on *Euomphalus*. In the centre of syncline, at M 6–7, and immediately S. of C.G. fault (M 10), in beds well exposed owing to their strike being parallel to the coast for about 200 yards.
(*b*) *Camarotoechia* beds. M 7 and M 11.
(*c*) *Schelwienella* bed. M 7 and M 12 β. (Indicated in the map by a chain-dot line.)
(*d*) *Athyris* bed. M 7 and M 12.
(*e*) *Schelwienella* bed. M 7 and M 12 *a*.

M 8 contains abundant *Syringothyris carteri*, and M 9 *Athyris glabristria*. These beds should be repeated at M 12 *x*. The latter beds are heavily covered by algae and animal growths, so that it is impossible to collect thoroughly. After some trouble three fossiliferous layers were found, two of which produced only *Syringothyris carteri*; the other (and lowest, uncovered in the Laminaria zone during a spring tide) gave a few specimens of *Athyris glabristria*.

The spacing of the beds (*a*) to (*e*) in the two series, as well as their order, is in agreement.

Block H (M 13). 240 feet = C_1.

Abundant—

Caninia cornucopiae, Mich., Carruthers.
(Mostly in "*cornu-bovis*" stage.)
Zaphrentis densa, Carruthers.
Densiphyllum nodosum, L. B. Smyth.
Michelinia cf. *tenuisepta*, Phill.
Spirifer aff. *clathratus*, McCoy, Vau.

Less common—

Amplexus coralloides, Sow.
Cyathaxonia cornu, Mich.
Michelinia gracilis, sp. nov.
Vaughania cleistoporoides, Garwood.
Zaphrentis omaliusi, Ed. & H., Carruthers.
„ *junctoseptata*, sp. nov.
Caninia cylindrica, Scouler.
Lophophyllum cf. *costatum*, McCoy.
Productus cf. *concinnus* (the St. Doulagh's form).
Pustula sp.
Chonetes squamata, L. B. Smyth.
Leptaena analoga, Phill.
Schelwienella sp.
Spirifer princeps, McCoy. ?
Martinia pinguis, Sow.
Spiriferina octoplicata, Mut. δ, Vau.
Athyris cf. *glabristria* (shallow sinus).
Rhipidomella Michelini, L'Ev.
"*Rhynchonella*," sp.

Correlation of beds South of Carrickhill Fault.

These beds are characterized by the abundance of *Caninia cornucopiae* ("*cornu-bovis*" stage) and *Spirifer clathratus*. *Zaphrentis densa*, *Michelinia* cf. *tenuisepta*, and *Martinia pinguis* are also fairly common. This agrees with γ of Burrington,[1] except in the matter of *Spirifer clathratus*, which, however, is the dominant Spirifer in γ of Belgium.[2]

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[1] Reynolds and Vaughan, Q. J. G. S., vol. lxvii, 1911 ("Burrington Paper"), p. 366.
[2] Vaughan, Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), p. 11.

Now we must place these beds either below all others in the section, i.e. low in Z, or above all, i.e. in C.

We have seen that the evidence from structure is in favour of the latter, i.e. down-throw to the south (see p. 10.) The following facts seem to me to settle the matter in favour of this interpretation:—

1. Two specimens of *Caninia cylindrica*, Scouler, were found: one near the middle, the other in the lowest exposed beds.

2. At M 13*d*, the lowest beds of the group under consideration, was found a fragmentary pedicle valve, about 40 mm. in length, which agrees with *Spirifer princeps*, McCoy, in its shape, its broad, flat ribs splitting into two unequal parts, and its fine reticulate pattern. This species is characteristic of the Tournaisian knolls ($\gamma - C_1$) of Belgium and Ireland, e.g. St. Doulagh's, County Dublin.

3. *Productus* cf. *concinnus* agrees perfectly with a form common at St. Doulagh's. The Producti found elsewhere in the section do not.

4. *Spiriferina octoplicata* has rounded cardinal angles and strong lateral ribs, as in Mut. δ, Vau.

5. *Michelinia* cf. *tenuisepta* and *Chonetes squamata* occur in C of Rush.

6. *Lophophyllum* suggests the higher, rather than the lower, level.

The evidence for regarding the M 13 beds as the highest in the section may be tabulated as follows:—

(*a*) The structure immediately at the fault (see p. 10).

(*b*) The direction of throw of neighbouring parallel dislocations (p. 10).

(*c*) Agreement with the railway fault in direction and amount of throw (p. 11).

(*d*) The fauna, just stated.

The only evidence against this is the similarity in lithology of M 13 to the "Lower Limestone Shales" of the S. of Ireland and S. Wales (see above, p. 11).

The thickness of the beds exposed N. of the Carrickhill fault is about 780 feet. The stratigraphical throw of the fault therefore must be at least 780 feet + the unknown (but probably small) thickness of beds cut out by the N. fault.

CORRELATION WITH RUSH AND WITH THE N. W. PROVINCE.

Owing to considerable difference in the fauna, close correlation with Rush could not be made. The whole of the Malahide exposure seems to be equivalent to part of the Rush Slates, $Z_2 - C_1$ (see L. B. Smyth, Proc. R. Dub. Soc., vol. xiv (N.S.), p. 535.

The Malahide beds resemble the *Solenopora* sub-zone ($\gamma - C_1$) of the N.W. Prov. in the abundance of *Athyris glabristria* and the occurrence of *Vaughania cleistoporoides*. Several other species, too, are common to both (see Garwood, Q.J.G.S., vol. lxviii, 1912, p. 460).

III. Palaeontological Notes.

Michelinia gracilis, sp. nov. (Pl. I, fig. 5, and text fig. 1)

M 13 = C_1.

Description.—Corallum of two to four long, flexuous, tubular corallites. Greatest length observed 5 cm., but the specimen was incomplete. Diameter of largest corallites 5 mm. Epitheca minutely wrinkled transversely. Grouping of tubes often, but not always, in one plane, recalling *Halysites*. Tubes usually in contact, but sometimes diverging near their extremities. Tabulae numerous, convex upwards, mostly complete, but often running together. No trace of septa. Mural pores few, irregularly distributed. When a corallite first appears it is D-shaped, or, if added between two others, triangular. In either case, the common wall is slightly convex towards the older corallite.

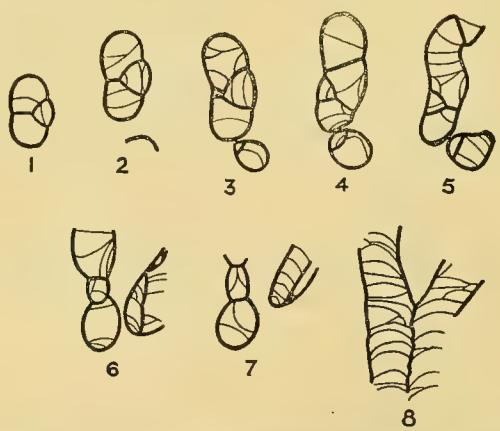


Fig. 1.—*Michelinia gracilis*, sp. nov. 1–7, serial section of one specimen; 8, longitudinal section of another specimen, showing divarication. Natural size.

Comparison.—I had assigned this coral provisionally to *Beaumontia* until mural pores were proved. The tabulae are exactly as in *B. egertoni*, M.-Ed. & H., and in the divergence of the corallites it recalls *B. laxa* M'Coy.

Michelinia aff. *megastoma*, Phill.

M 4 and top of M 5 = Z_2 – C_1.

Description.—Height up to at least 20 mm. Calyces 20 or more, subequal, shallow, with septal striae. Average diameter of calyces, 7 or 8 mm. Abundant vesicular tissue extending from base often up to height of 17 mm. Stereoplasm moderate, not obliterating vesicular tissue. Other characters as in *M. megastoma*. Near the top of M 5 one bed contains, in addition to the larger colonies, young ones in various stages, the smallest found having but four corallites.

Comparisons.—It agrees very well with de Koninck's illustration of *M. megastoma* in his "Recherches sur les Animaux Fossiles du Terr. Carb. de la Belgique," Pl. XIII, figs. 3–3*b*.

It is evidently the form referred by Vaughan[1] to his *M. megastoma* (Phill.), Mut. Z_2. I find it to differ, however, from his description as follows:—Number of corallites greater, calyces shallow, vesicular tissue abundant, and *not* nearly concealed by stereoplasm.

From *M. megastoma* of the Rush Conglomerate (C_2) it seems to differ only in dimensions, the average calyx diameter of the Rush form being 10–12 mm. The present form is probably an earlier mutation of that found at Rush, and possibly intermediate between it and Vaughan's Mut. Z_2. Or it may be a variety (i.e. contemporary close relative) of Mut. Z_2; or even a local form of Mut. Z_2 due to environment.

Zaphrentis.

The commonest[2] species at Malahide is *Z. densa*, Carruthers, which is common at many levels throughout the exposure. A few specimens of the typical *Z. omaliusi*, Ed. & H., were identified. *Z. ambigua*, Carruthers, was not found. *Z. delanouei*, Ed. & H., s.s., occurs from M 3 down to M 9, and is common at M 5 and M 11. A section below the calyx of an M 5 specimen has a diameter of 10 mm. *Z. parallela*, Carruthers, was noted at M 4 (top) and M 11.

Zaphrentis junctoseptata, sp. nov. (Pl. I, figs. 1–4).

M 13 = C_1.

Description.—Irregularly cornute. Often one or more strong constrictions. Epitheca finely wrinkled. Well marked, flattened costae. Length up to about 20 mm. Diameter of calyx about 9 mm. Major septa reach the centre, except just below a tabula. Cardinal fossula on convex side, bounded

[1] Q. J. G. S., vol. lxvii, 1911 ("Burrington Paper"), p. 371.

[2] Cf. Vaughan, Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), p. 34.

by two major septa. Cardinal septum as long as the rest. Septa more or less concave to cardinal fossula. Minor septa long, each leaning against a major on the side remote from the cardinal fossula. The counter septum thus has two minors leaning against it.

The tabulae are irregular, often very oblique. This produces the grouping of septa seen, e.g. in Pl. I, fig. 2, and to a less degree in figs. 1*a* and 4*a*. Symmetrical sections are uncommon. The obliquity of the tabulae has no relation to the position of the fossula (cf. Pl. I, figs. 1*a* and 2). Rejuvenescence was observed in some specimens.

The youngest section obtained (3·5 mm. diam.) resembles a young *Z. omaliusi*, except that already there are two minor septa leaning against the counter septum, and of nearly half its length. The other minors are barely indicated.

Comparisons.—This coral is convergent in septal plan with *Cyathaxonia cornu*, with which it is associated.

It bears a strong resemblance to *Zaphrentis cassedayi*, M.-Ed.,[1] but is distinguished therefrom by the absence of spines on the epitheca.

From *Z. delépini*, Vau.,[2] it is easily separated by the great development of all the minor septa. In other respects there is considerable resemblance.

It differs from *Z. vaughani*, Douglas,[3] in this same way, and also in the following points:—The fossula is on the convex side, and is bounded by a single septum on each side; the cardinal septum reaches the centre; the septa are concave to the fossula.

Endophyllum irregulare, sp. nov. (Pl. I, figs. 7–9.)

M 2, 4 = C_1.

Description.—Length 55 mm. Growth very irregular. Strong thickenings at intervals.

Transverse section, mature.—Diameter 17 mm. Central area occupied by tabular intersections only. The medial area contains 37 major septa, very unequal in length, sometimes reaching nearly to the centre, sometimes reduced to short spikes, not thickened, often flexuous. Cardinal septum doubtfully to be distinguished. Minor septa appear as teeth on the outer wall. Outer area composed of vesicles which may all be large and loose, with tooth-like septal projections on their outer walls; or may nearly all be interseptal, so that most of the septa reach the outer wall without

[1] H. Milne Edwards, Histoire Naturelle des Coralliaires, 1857–60, Pl. G 1, fig 2.

[2] A. Vaughan, Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), p. 34, and Pl. iv, figs. 3 and 4.

[3] J. A. Douglas, Q. J. G. S., vol. lxv, 1909, p. 577, and Pl. xxvii, fig. 11. A. Vaughan, Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), p. 35, and Pl. iv, fig 7*.

discontinuity. Any intermediate state may occur, and the extremes may be shown by closely contiguous sections of one individual. The outer area is usually more developed on one side, and may be entirely absent from the other.

Transverse section, young.—Only major septa present, not reaching the centre, sometimes very short. No outer area. Cardinal septum may be shorter than the rest.

Longitudinal section.—Tabulae close, wide, and flat, bent down at the side, where they meet the marginal vesicles.

Comparisons.—This coral closely resembles the Upper Devonian *E. priscum*, Münster, as figured by Frech.[1] The latter differs from our form in having minor septa on its inner wall, and in its more regular habit.

From *E. burringtonense*, Vau,[2] the present species differs in the absence of the peculiar grouping of the septa in that form, and in the smaller development of minor septa.

Vaughan records his species from Malahide, but I have only found the form described above.

It is interesting to compare—

Endophyllum irregulare, sp. nov., C_1, Malahide.
Thysanophyllum pseudovermiculare, McCoy, C_{1-2}, N.W.P.[3]
Endophyllum cf. *pseudovermiculare*, Vaughan, lower S, Belgium.[4]

Lophophyllum cf. *costatum*, McCoy. (Pl. I, fig. 6).

M 13 = C_1.

Description.—Only two imperfect specimens were found, and transverse sections alone obtained. Transverse section:—Diameter of calyx, 10·5 mm.; major septa, 23 in one specimen, 20 in the other, reaching about half way to the centre. Minor septa barely indicated at rim of calyx. Cardinal septum shorter than the rest. Septa in cardinal quadrants thickened so as to be in contact. Tabular intersections, 3 or 4. Columella continuous with counter septum, very slightly thickened, with 4 to 6 rudimentary lamellae on each side. In the calyx the columella forms a strongly thickened boss, oval in section, 4 × 2·5 mm. One row of vesicles occurs on the calyx wall.

Comparison.—This coral may well be a precursor of that described by Wilmore as *Lophophyllum costatum*, McCoy,[5] from D_3 of the Midlands

[1] Zeitsch. Deutsch. Geol. Gesellsch., vol. xxxvii, 1885, p. 76, Pl. vii, fig. 2, and Pl. x, fig. 2.

[2] Reynolds and Vaughan, Q. J. G. S., vol. lxvii, 1911 ("Burrington Paper"), p. 377, and Pl. xxx, fig. 4.

[3] Garwood, Q. J. G. S., vol. lxviii, 1912, p. 562, and Pl. xlix, fig. 2.

[4] Q. J. G. S., vol. lxxi, 1915 ("Belgian Paper"), p. 39, and Pl. v, fig. 3.

[5] Q. J. G. S., vol. lxvi, 1910, p. 573, and Pl. xl, figs. 1-4.

of England. It differs from that species as follows:—Smaller size; major septa fewer, shorter; minor septa scarcely developed; vesicular zone rudimentary.

Camarotoechia aff. *mitcheldeanensis*, Vau.

This only differs from Vaughan's species in having usually 4 ribs on the fold and 3 in the sinus, and in its slightly larger size. The internal structure is essentially the same.

Athyris cf. *glabristria*, Phill.

There are two distinct forms included under this description:—

(*a*) A gibbous shell, whose fold and sinus appear early and become extremely marked with age. It seems to agree with the one figured by Garwood as the index of his zone A.[1]

(*b*) A larger, more depressed shell, whose fold and sinus appear late, and only cause a slight undulation in the valve intersection. This is evidently the form referred to by Vaughan as *A. lamellosa-glabristria*.[2]

Both forms vary considerably, but I have not found a full-grown individual that could not be unhesitatingly referred to either (*a*) or (*b*). Both are usually transverse. The ornament of both is the same, and is like Davidson's Plate XVIII, fig. 10, there being about two fringes per millimetre. The narrow lamellae, where the fringe is stripped off, show an alternation in strength, one, two, or three weak ones occurring between two stronger ones. Strongly marked growth halts, as noted by Vaughan, occur in both.

Form *a* is abundant at two different levels—M 1 and M 8, 9 (and their repetition M 12). Form *b* is abundant and large throughout M 1, 2, 3, and 4.

Seminula cf. *ambigua*, Sow.

M 5 = Z_2.

This is a very small shell. The largest specimen had the dimensions:—Length, 12 mm.; width, 14 mm.; depth, 5 mm. The proportions are approximately as in Davidson, Brit. Carb. Brach., Plate XV, fig. 17, but the beak is sharper and less arched.

Previous Work on the Section.

The late Dr. Vaughan intended at one time to publish an account of the Malahide fauna. He has referred to it in the Burrington and Belgian papers.[3] In these the following fossils and horizons are mentioned as occurring at Malahide:—

[1] Proc. Geol. Assoc., vol. xxvii, Pl. xii, fig. 3.

[2] Q. J. G. S., vol. lxxi, 1915 ('Belgian Paper), p. 16.

[3] Reynolds and Vaughan, Q. J. G. S., vol. lxvii, 1911. Vaughan, Q. J. G. S., vol. lxxi, 1915.

Burrington paper (1911)—

Endophyllum burringtonense. Vau. γ (p. 379).
Michelinia megastoma. Mut. Z_2. Z_2 (p. 371).

Belgian paper (1915)—

Athyris lamellosa-glabristria. C_1 (p. 16).
Syringothyris laminosa. C_1 (p. 16 and pl. vi, fig. 1; p. 43, foot-note).
Michelinia, *Syringopora*, and the giant *Conocardium.* C_1 (p. 16).
Zaphrentis delanouei and *Z. densa.* C_1 (p. 16, foot-note).
Zaphrentis delanouei and Mut. *parallela.* γ (p. 34).

Before commencing work I had at my disposal, in addition to the references just quoted, slides given me some years ago by Dr. Vaughan labelled thus :—

Zaphrentis delanouei. Z_1 Malahide.
Cyathaxonia cornu. S. of fault, Malahide ≡ Rush Slates.
Michelinia cf. *tenuisepta.* Rush Slates, Malahide.
Zaphrentis omaliusi, var. *densa.* Carr. Z_2 Malahide.
Densiphyllum. Malahide, S. of fault ≡ Rush Slates.
(This is *D. nodosum.* See Proc., R. Dub. Soc., vol. xiv (N.S.), p. 556.)

When the work for this paper was nearly complete, I was enabled, through the kindness of Professor S. H. Reynolds, to look through part of Vaughan's Malahide collection which had come into his possession. It is small, and contains nothing I had not already found. Besides it is obviously not complete as, e.g., *Endophyllum burringtonense* is absent. There is no key to the symbols he used, and I could only correlate them with mine in a few cases. It may interest some if I set them out. The second column contains correlations found on some of the labelled specimens.

P	C_1 *Laminosa* beds	
O		
N		
M		
L	γ	
K	base of γ	
J	Z_2	= M 5
I = J		
H		
G		
F	Z_1	= M 8
E	Z_1	= M 9
D		
C	Z_1	
B	base of Z_1, beds S. of fault ≡ Rush Slates 6*a*, 6*b*.	= M 13
A		

It appears from this that the beds S. of Carrickhill fault were regarded as the lowest in the exposure.

SUMMARY OF THE CHIEF POINTS IN THE PAPER.

1. There are *three* faults of importance in the exposure, not only *one*, as previously believed.
2. The southern (Carrickhill) fault has the down-throw to the south, not to the north.
3. Correlation is made with C_1 – Z of the S.W. Province of England.
4. Three new species are described and figured, namely:—*Zaphrentis junctoseptata, Michelinia gracilis, Endophyllum irregulare.*
5. Another form, which appears to be new, is described and figured, of which sufficient material could not be obtained for a satisfactory study, namely:—*Lophophyllum* cf. *costatum*, McCoy.
6. A *Seminula* (cf. *ambigua*) is reported in a Z_2 fauna.

PLATE I.—CORALS FROM THE "C" ZONE AT MALAHIDE.

FIGS. 1 to 4. *Zaphrentis junctoseptata*, sp. nov. M 13 (p. 19).

1, a, b, c. Photographs of three transverse sections from the same specimen. In 1c note the presence of two minors leaning against the counter septum, although the majors have not yet all appeared. × 2·7.
2. Camera lucida drawing of mature transverse section of a second specimen. × 5.
3. Photograph of mature transverse section of a third specimen. × 2·7.
4, a, b. Camera lucida drawings of two transverse sections of a fourth specimen. × 5.

FIG. 5. *Michelinia gracilis*, sp. nov. M 13 (p. 18).

A weathered specimen, consisting of two corallites, on a slab of limestone. Opposite the arrow a portion of the wrinkled epitheca is preserved. Just below this, some of the tabulae are exposed. × 0·6.

FIG. 6. *Lophophyllum* cf. *costatum*, M'Coy. M 13 (p. 21).

Transverse section just below floor of calyx. × 2·7.

FIGS. 7 to 9. *Endophyllum irregulare*, sp. nov. M 2 (p. 20).

7. Drawing of a specimen showing external characters. × 0·5.
8, a, b, c. Three sections from another specimen. × 2·7.
9. Portion of longitudinal section of a third specimen. × 2·7.

FIG. 10. *Caninia cylindrica*, Scouler. M 13.

Transverse section of immature stage. This is from the specimen referred to on page 17 as occurring at "near the middle" of M 13. It is figured because this early stage seems to be rather rarely found, and it is larger than the corresponding stage figured by Salée in "Le Genre *Caninia*," Nouv. Mém. Soc. belge Géol., Mém. No. 3 (1910). × 2·7.

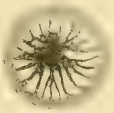
PLATE II.

The left-hand figure is a plan of the outcrop at high-water level. The topography is reduced from the Ordnance Survey 25-inch map.

The right-hand figure is a horizontal section along the line marked on the plan.

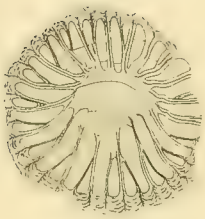
E, F, G, H. Blocks into which the section is divided by the three faults.
M 1–M 13. Symbols for groups of beds, used in labelling the fossils.
H (= M 13) is a higher horizon than M 1.
G is a repetition of F.
M 4d. A bed taken as the top of the "*Zaphrentis*" zone.
M 12, α and β. Two beds of *Schelwienella*.
M 12β, in G, and the same bed in F, are marked by a chain-dot line.

4a.

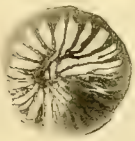


1b.

1c.

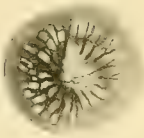


2.



1a.

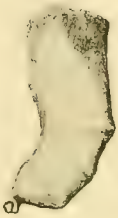
4b.



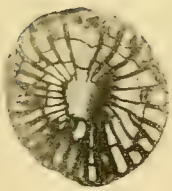
3.

5.

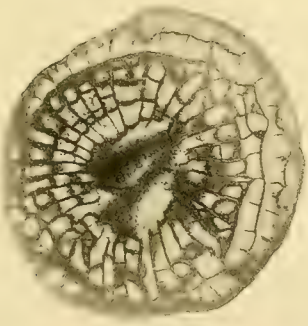
6.



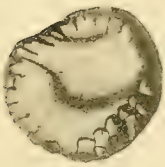
7.



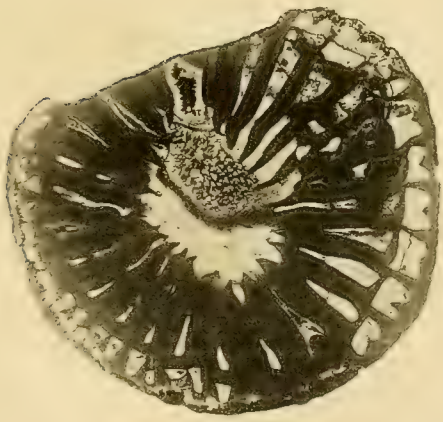
8b.



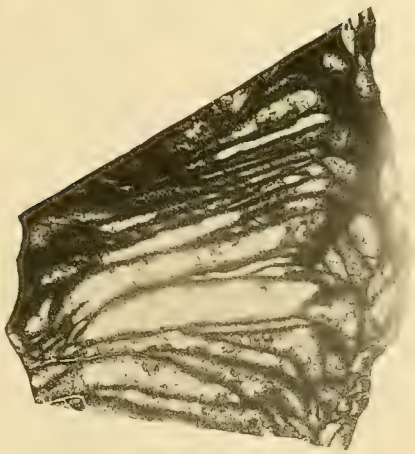
8a.



8c.



10.



9.

Bemrose, Collo., Derby.

PLATE II.

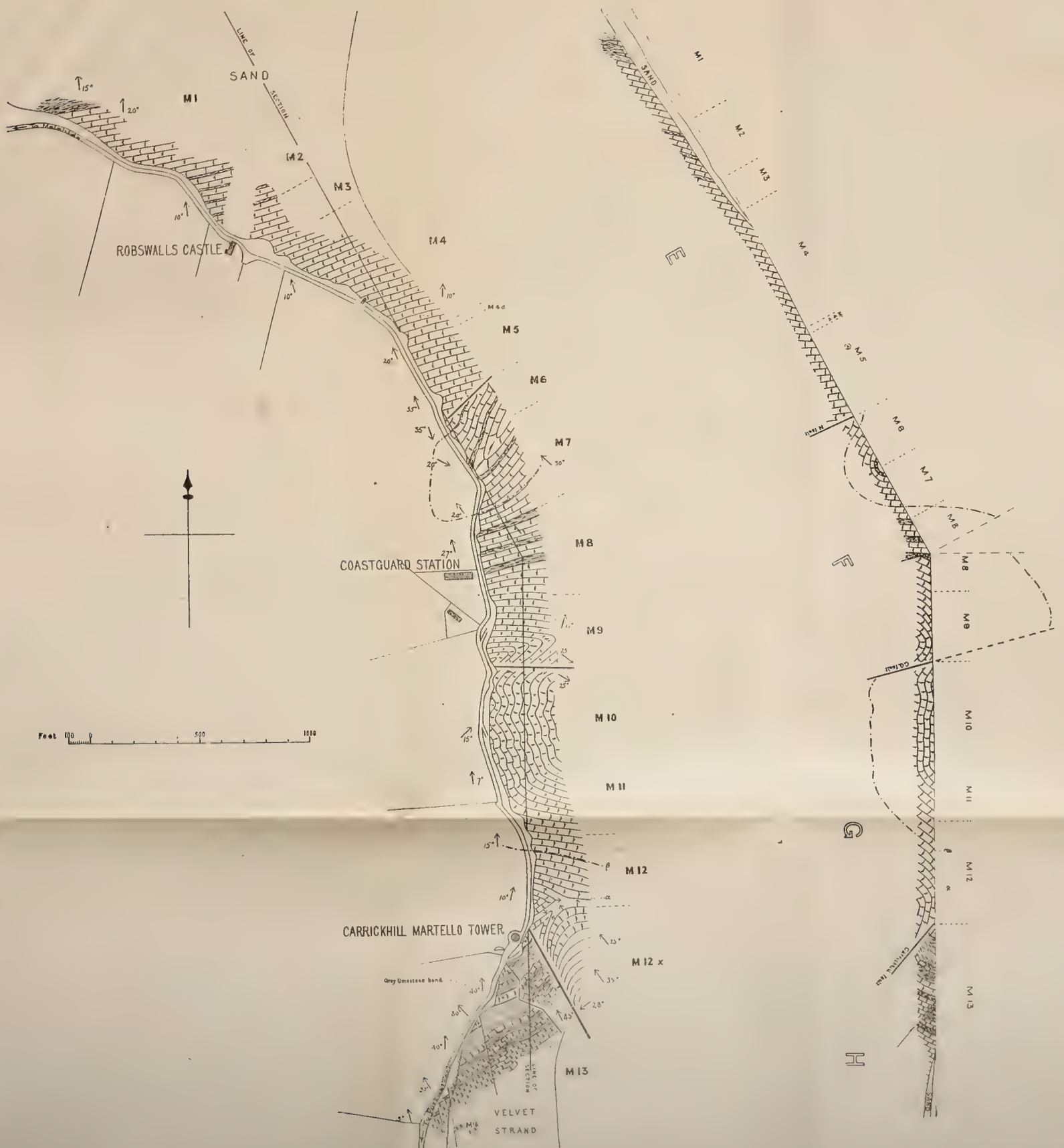


FIG. 1. CARBONIFEROUS COAST SECTION AT MALAHIDE, CO. DUBLIN

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1. A Cryoscopic Method for the Estimation of Sucrose. By Henry H. Dixon, sc.d., f.r.s., and T. G. Mason, m.a., sc.b. (January, 1920.) 6*d*.

2. The Carboniferous Coast-Section at Malahide, Co. Dublin. By Louis B. Smyth, b.a., sc.b. (January, 1920.) 1*s*.

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THE APPLICATION OF THE FOOD-UNIT METHOD TO THE FATTENING OF CATTLE.

BY

JAMES WILSON, M.A., B.Sc.,

PROFESSOR OF AGRICULTURE IN THE ROYAL COLLEGE OF SCIENCE, DUBLIN.

Smithsonian Institution
MAR 5 1921
National Museum

(PLATES III., IV.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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MAR 5 1921

III.

THE APPLICATION OF THE FOOD-UNIT METHOD TO THE FATTENING OF CATTLE.

By JAMES WILSON, M.A., B.Sc.,
Professor of Agriculture in the Royal College of Science, Dublin.

(Plates III., IV.)

Read January 27. Published February 20, 1920.

During the last thirty years the Danes and Swedes have greatly advanced our knowledge of the use of feeding-stuffs for certain kinds of live-stock. They have worked chiefly at two sides of the problem, namely, at determining (1) the relative feeding values of the usual feeding stuffs, and (2) the quantity of food required, during all stages of lactation and non-lactation, by cows of different sizes and milk-yielding capacities. Under the first head, they have found that, when they form a fair—i.e., not extreme—proportion of the total ration, 2·5 lbs. of meadow hay, 4 lbs. of oat straw, 10 lbs. of mangels, and 1·2 lb. of oats have, on the average, the same feeding value as a pound of barley. Then, if a pound of barley be taken as the food-unit,[1] it can be said that 2·5 lbs. of meadow hay, 4 lbs. of oat straw, 10 lbs. of mangels, and 1·2 lb. of oats each contain a food-unit. And, if a cow consume 20 lbs. of meadow hay, 80 lbs. of mangels, and 6 lbs. of oats, it can be said that she consumes 21 food-units:—$20 \div 2{\cdot}5 + 80 \div 10 + 6 \div 1{\cdot}2 = 8 + 8 + 5 = 21$.

Under the second head, they have found that cows' needs vary with their weight, advance in pregnancy, and milk yield. The food-units necessary to maintain barren cows or heifers of different weight, or a bullock, for that matter, in constant condition—i.e., becoming neither fatter nor leaner—are approximately as follows:—

Live Weights.	Food Units.
7 cwts.	5·5
8 ,,	6·25
9 ,,	7
10 ,,	7·75
11 ,,	8·5

Shortly after becoming in calf, the cow's needs increase till just upon calving time, when, for all weights alike, three more units are necessary. After calving, another half unit is necessary for the first ten pounds, and thereafter

[1] The Swedes take a kilogramme of barley as the unit.

a third of a unit for every additional pound of milk. These findings are expressed in the diagram (Plate III.).

The use of this diagram may be illustrated thus:—A nine hundredweight cow giving five gallons of milk needs about 24 food-units a day. This number might be extracted from 96 pounds (24 × 4) of oat straw, or 60 pounds (24 × 2·5) of meadow hay; but, since no cow can deal with even the smaller of these quantities in a day, the total bulk of the ration must be brought down to the cow's capacity by reducing the long fodder and substituting something which, by being readily digestible, passes quickly from the stomach, or, by having its nutritive ingredients highly concentrated, takes up little space. The necessary food-units might also be extracted from 240 pounds (24 × 10) of mangels, but, though some cows might consume this quantity, few could do so and remain in good health. Besides, the digestibility of the whole ration is lowered when roots or long fodder or both are fed in large quantity. Thus, to keep the whole ration within the stomach-capacity, a cow giving a large yield of milk must have concentrated foods in addition to long fodder and roots. The following may be taken as an example ration for a five-gallon cow weighing about 9 cwts., in which the limits of total bulk are not overstepped:—

Meadow Hay,	17½ lbs.	=	7 units.
Mangels,	70 „	=	7 „
Concentrates,	10 „	=	10 „
			24

As the cow's yield decreases, or for a lower-yielding cow, straw may be substituted for hay, and, first, concentrates then mangels decreased till, when she is dry and far from calving time or not in calf at all, the ration may consist of straw alone. Since concentrated feeding stuffs came into use, in the first half of the nineteenth century, and winter fattening of stock became possible, many fattening experiments have been carried out in England and Scotland, some of which have been described in the Journals of the English and Scotch Agricultural Societies, the Journal of the Board of Agriculture, and reports sent out by agricultural colleges. A very carefully compiled digest of these experiments was published in the 1909 volume of the "Transactions of the Highland and Agricultural Society of Scotland," by Mr. Herbert Ingle, B.Sc. For each experiment Mr. Ingle gives, among others, the following data:—

1. The experimenter's name.
2. The date of the experiment.

3. The age, breed, and sex of the experimental animals.

4. The duration of the experiment.

5. Details of the average ration.

6. The total digestible albuminoids in the ration.

7. The starch-equivalents of the digestible fats, carbohydrates, amides, and fibre in each ration.

8. The total digestible matter and the total digestible albuminoids and starch-equivalent of the rest of the digestible matter in each ration per 1000 lbs. live weight of the experimental animals.

9. The albuminoid ratio of each ration.

10. The digestible matter consumed for every pound of live weight increase.

11. The daily live weight increase of the animals.

12. The average live weight of the animals during the experiment.

Early in the latter half of the nineteenth century the theory was propounded that the efficiency of a ration depended upon its albuminoid ratio, that is, upon the proportion of its digestible albuminoids to the digestible carbohydrates, fats, and fibre together. Investigators like Wolff and Kühn suggested ratios from 1 : 5 to 1 : 6 for fattening stock ; but, though this had the effect of raising the money value of albumen far beyond what its fattening power could have justified, the albuminoid ratio theory never seriously affected British stock fatteners, and towards the end of the century it began to lose credit even among those who had been taught by its chief exponents. Mr. Ingle's digest shows that it was anything but a sure and certain guide.

It was then seen by some investigators that even the total amount of dry matter in a mixed ration and, still more, the total digestible matter was a better measure of the ration's efficiency. Of course, it was realized that every animal's albuminous waste must be made good and its needs supplied for the production of growing tissue; but, when Kellner's work became known, it was obvious that his proposal was still better, namely, that, when sufficient albumen has been fed to meet albuminous waste and produce growing tissue, the test for the rest of the ration should be the proportion it contains of digestible starch, fat, and fibre : the two latter being reduced to their energy-producing equivalent in starch, and the three together called the " starch equivalent."

But few farmers have the technical knowledge with which alone Kellner's proposals are to be adapted to a particular case; still fewer when they are expressed in calories.

In the experimental work so far carried out, one important question has not been answered. No experimenter has definitely determined the maximum daily increase bullocks are capable of making and the food necessary to produce it, and farmers, being more immediately concerned, perhaps, with the mere conversion of straw and roots into manure, have not asked the question. The need for knowing the possible maximum increase may not be obvious, but it is none the less important, for, since a certain portion of his daily ration—roughly, about a third in the case of a fattening bullock, and frequently nearly the whole, sometimes more, in that of a store bullock —is required for mere maintenance of life, while the rest goes towards increase in live weight, it is clear that the bullock which fattens the quickest, and so shortens the expenditure in mere maintenance, requires, over all, the smallest amount of food for the beef produced.

Missing this question, experimenters, as a rule, have usually sought to deal merely with questions of the moment which occurred to farmers in their customary practice. When turnips came into use, but before the introduction of concentrates, the first systematic experiments (Thaer's) were devised to find how many turnips should be substituted for the hay withdrawn from the old ration of hay alone and have the bullocks continue in the old condition. In time, it was found that too many turnips could be fed, but nobody found what might be called the limit of safety. Had some one determined the optimum proportions of straw, or hay, or both, with turnips, it is possible that, when concentrates were introduced, experimenters might have tried to determine how much extra live weight was produced by the addition of concentrates, and then raised the question: what is the possible live weight increase? British experimenters have followed no clear policy, and so no crucial question has been sufficiently investigated to become the starting-point for a successor. For the most part, the experiments have been mere trials of varying quantities of roots or straw, or of one or more food-stuffs against each other.

By using the Scandinavian system of food-units, it may be possible, however, to make a great part of the recorded British experiments complementary to each other, and to draw some general conclusions which may be approximately accurate and, so far, useful. This may be done by calculating the food-units contained in the rations and plotting them against the daily increases each ration produced, as in the diagram (Plate IV.). To bring out the point that the food consumed rises with their weights, the experimental animals have been divided into groups of ascending weights and the plottings for each group set out in separate sets. The weights are the averages during the experimental periods.

In order to avoid extremes, only experiments which lasted over 70 and under 170 days have been made use of.

Certain experiments could not be used because their food-ingredients were too loosely described. "Roots," for instance, may be of several kinds. In one set of experiments, "roots" were found, from the original paper, to be almost equal quantities of mangels and swedes, and the food-units are calculated on this understanding. In some experiments "common cotton cake" was fed, and, on reference to the compositions given in the original papers, this was found to be undecorticated cotton cake. One important series of experiments could not be used at all, because the amount of straw consumed was not stated.

One extremely large, probably an impossible, ration, and another set, in which the gains are suspiciously large for the food consumed, have been omitted.

Modern experimenters usually have the animals fasted before weighing them. It is not certain that the older experimenters had this done, but, as they are likely to have followed the same practice at both ends of the fattening period, the errors resulting from weighing the animals unfasted are not vicious when different sets of experiments are being used together. There are more serious causes of variation which cannot be taken into account, as, e.g., the varying capacity of cattlemen; but the results in one direction may reasonably be assumed to be cancelled by those in another. This remark applies equally, no doubt, to the experimenters themselves, and to some extent reduces the value of the deductions to be made from their work.

When the data had been plotted, as in the diagram, it was obvious that a straight line could not be drawn through the plottings by the eye. Then the average food-units consumed per group and the daily gains produced were calculated and plotted on the diagram in crosses. The spaced line which joins these crosses, however, is neither straight nor regularly curved, and, if it were to be used, the factors which make it crooked would have had to be found and allowed for. Therefore another line must be found.

The ideal line would be that which should show, for all weights of cattle, the highest possible daily gains and the lowest possible food-units necessary to produce them; but such a line cannot yet be drawn. The highest daily gain shown in the diagram is 3·1 lbs., made by a lot of 12-cwt. bullocks, upon 19·8 food-units a day; but we do not know that this is the possible limit.

A Scotch experimenter (Dr. J. W. Paterson) had a lot of bullocks which made 3·66 lbs. a day, over a period of eighty-eight days, upon pasture, cake, and meal; and, last summer, at Clonakilty Agricultural Station, four bullocks,

over a period of six weeks, made a daily gain of 3·75 lbs. upon pasture alone. One of the four bullocks made four pounds a day. It may be that similar gains are not impossible upon long fodder, roots, and concentrates, and the units necessary to produce them may be less than in the proportion of 19·8 units for 3·1 lbs. increase.

All that can be done in the meantime is to indicate the daily gains shown to be readily attainable—not the maximum—with a reasonable—not the minimum—number of food-units. This is done by the continuous straight line drawn across the diagram. It will be seen that this line runs well above, or just under, the numbers of food-units which have produced daily gains of two pounds or over, namely:—

14·25	units for	6-cwt.	beasts.
15	„	7-cwt.	„
15·75	„	8-cwt.	„
16·5	„	9-cwt.	„
17·25	„	10-cwt.	„
18	„	11-cwt.	„
18·75	„	12-cwt.	„

But this line must not be used without the caution that the experiments show the rations to have very variable efficiencies. It will be seen that in every group a large number of the rations do not produce two pounds a day. If lines be drawn upwards through the average of the dots in every group, the dots which fall to the left will indicate the less effective, those to the right the more effective, rations. Not only so, but the distances of the dots from the upright lines may be taken as indications of the efficiency of the rations concerned. On this understanding the following table shows the relative inefficiencies (–) and efficiencies (+) of the rations in each group:—

NOTE:—The rations marked T received in addition small quantities of treacle or molasses.

No.	Live Weight.	Food-units consumed.	Daily gain. lbs.	Ration in lbs.				Relative Efficiency.
				Straw.	Hay.	Roots.	Concentrates.	
1		11·59	1·51	0	8·5	26·5	4·5	− 5
2		11·59	1·67	0	8·5	26·5	4·5	− 3
3	6 cwts.	12·34	1·85	0	8	46	4·03	− 2
4		12·34	1·90	0	8	46	4·03T	− 1
5		11·37	2·07	0	8·5	26·5	4·5	+ 2
6		15·34	1·73	0	7·7	56	5·56T	− 3
7		14·14	1·69	0	10·4	28	6·06T	− 2
8		16·14	1·87	0	12·5	42	7	− 2
9		16·07	1·81	0	12·5	42	7	− 2
10		16·15	1·87	0	12·5	42	6	− 2
11	7 cwts.	13·67	1·68	0	7·7	65	3·4	− 2
12		13·67	1·76	0	7·7	65	3·4	− 1
13		14·18	1·96	5·77	7	50	4·37	0
14		14·18	1·96	5·77	7	50	4·36	0
15		12·78	1·85	0	14·63	0	6 T	+ 1
16		14·06	2·05	0	11·58	28	5·52T	+ 2
17		18·11	1·44	8	0	110	4	− 8
18		12·1	·96	0	0	109	0	− 6
19		16	1·42	13·6	0	0	10·4	− 6
20		16·35	1·71	0	12·5	42	6	− 3
21		16·04	1·63	0	14	56	4·5	− 3
22	8 cwts.	15·53	1·73	0	13·8	56	4·58	− 2
23		15·24	1·82	0	13·8	56	3·82	− 1
24		16·58	2·14	10	5	50	6	+ 1
25		16·53	2·26	10	5	50	6	+ 2
26		16·3	2·21	1·57	7·44	73	5·36	+ 2
27		16·34	2·42	1·57	7·44	73	5·36	+ 4

No.	Live Weight.	Food-units consumed.	Daily gain. lbs.	Ration in lbs.				Relative Efficiency.
				Straw.	Hay.	Roots.	Concentrates.	
28		15·68	·88	7	0	126	0	− 10
29		20·19	1·49	7	0	130	4	− 10
30		20·08	1·43	3	7	100	5·3	− 9
31		16·80	1·16	0	7	126	0	− 9
32		21·96	1·72	4	4	105	8·84	− 8
33		20·27	1·57	7	0	130	3·67	− 8
34		23·48	1·93	4	4	105	8·85	− 7
35		14·65	1·11	8·5	0	50	7·25	− 7
36		21·72	1·81	4	4	105	8·86	− 7
37		18·41	1·43	7	0	150	0	− 7
38		17·75	1·38	3·75	8·25	95·5	3·49	− 6
39		20·08	1·78	3	7	100	5·3	− 6
40		17·75	1·49	3·75	8·25	95·5	3·49	− 6
41		17·22	1·48	5	0	114	3·02	− 6
42		16·77	1·47	8·16	0	112	3	− 6
43		16·92	1·43	10	0	75	5·3	− 6
44		20·08	1·81	3	7	100	5·3	− 5
45	9 cwts.	19·03	1·71	10	0	100	0	− 5
46		18·41	1·64	5	0	120	3·88	− 5
47		18·58	1·67	5	0	108	3·88	− 5
48		13·90	1·20	9·97	0	50	6·67	− 5
49		15·28	1·42	9·08	0	50	10	− 5
50		14·77	1·33	8·36	0	50	9·37	− 5
51		16·77	1·61	8·16	0	112	3	− 4
52		13·81	1·26	7·9	0	50	8·5	− 4
53		16·00	1·54	10	0	80	4	− 4
54		15·16	1·43	8	0	84	3·88	− 4
55		15·25	1·51	7	0	95	4	− 3
56		19·54	1·98	3·54	3·54	56	9·74	− 3
57		17·11	1·70	10	0	100	4	− 3
58		16·00	1·89	8	0	109	3	− 1
59		13·75	1·58	7	0	120	0	− 1
60		13·48	1·60	5	0	84	3·88	− 1
61		15·83	1·94	0	16	28	6·5	0
62		19·24	2·38	3·07	3·08	90	6·1	+ 1
63		19·30	2·42	3·78	3·78	56	9·74	+ 2

No.	Live Weight.	Food-units consumed.	Daily gain. lbs.	Ration in lbs.				Relative Efficiency.
				Straw.	Hay.	Roots.	Concentrates.	
64	10 cwts.	24·09	1·73	4	4	112	8·7	− 9
65		22·33	1·69	4	4	112	8·7	− 8
66		22·02	1·78	15	0	90	6	− 7
67		24·06	2·10	4	4	112	8·7	− 6
68		15·49	1·31	0	22	0	6	− 5
69		24·97	2·38	7	0	155	3	− 4
70		19·05	1·97	0	0	131·11	4·6	− 2
71		16·41	2·48	8	0	108·75	3	+ 5
72	11 cwts.	22·76	1·33	4	4	112	8·6	− 11
73		22·23	1·52	4	4	112	8·6	− 9
74		23·04	1·71	4	4	112	8·6	− 7
75		18·78	1·50	9·5	5	0	13 T	− 6
76		19·22	1·59	15	0	90	6	− 5
77		16·19	1·35	9·6	0	45	8	− 5
78		16·51	1·50	2·71	7·08	29	10·23	− 4
79		15·61	1·37	7	7	0	9 T	− 4
80		14·60	1·28	14·1	0	0	10	− 4
81		22·51	2·11	0	0	127·03	7·72	− 3
82		21·21	1·98	15	0	90	8·59	− 3
83		21·72	2·06	14	7	63	8	− 3
84		19·11	1·97	0	8·88	40·34	10·18	− 1
85		12·18	1·35	0	17	48·4	0	− 1
86		17·42	1·98	2·92	6·55	32·4	9·64	0
87		19·07	2·22	0	8·88	40	10·18	+ 1
88		22·24	2·60	14	7	63	8	+ 2
89		16·72	2·15	4	6·97	39·9	9	+ 3
90		16·68	2·35	4·1	6·9	39·5	9	+ 5
91		16·06	2·54	0	15·49	44·3	4·32	+ 7

No.	Live Weight.	Food-units consumed.	Daily gain. lbs.	Ration in lbs.				Relative Efficiency.
				Straw.	Hay.	Roots.	Concentrates.	
92	12 cwts.	23·11	1·64	9·5	5	82	12·5 T	~ 8
93		19·90	1·60	11	5·5	56	9·4 T	– 6
94		23·06	1·92	7	7	70	10·5	– 5
95		23·81	2·11	5	5	115	8·8	– 4
96		22·92	1·95	5	5	107	8·8	– 4
97		15·74	1·26	11	5·5	0	9·4 T	– 4
98		23·11	2·07	9·5	5	82	12·5 T	– 4
99		20·83	1·91	5·5	5·5	84	8·8	– 3
100		18·98	1·78	11	5·5	56	9·4 T	– 3
101		18·03	1·73	8	8	42	8·8	– 2
102		23·11	2·31	9·5	5	82	13·5	– 1
103		19·07	1·90	0	10	95	5·35	– 1
104		18·37	1·82	4	12	34·6	8·1	– 1
105		17·78	1·86	0	16·1	39·2	9·07	0
106		16·61	1·76	7	7	0	10·5 T	0
107		19·15	2·04	3·5	10·6	56·6	8·1	0
108		21·23	2·39	0	16·2	40·5	9·03	+ 1
109		19·02	2·20	0	14	45	8·19	+ 2
110		16·61	1·94	3·55	7·66	32·42	9·11	+ 2
111		19·07	2·38	0	10	95	5·35	+ 4
112		18·19	2·30	0	11	45	8	+ 4
113		17·95	2·38	3·82	7·03	32·2	9·76	+ 5
114		19·85	3·13	0	13·73	40·2	8·66	+ 10

In these experiments no lot was fed upon either long fodder alone or concentrates alone. One lot, No. 18, was fed on roots alone (109 lbs.), with an inefficiency which is represented by the figure – 6. Six lots were fed on long fodder and roots, always with minus efficiencies, namely:—

No.	Straw. lbs.	Hay. lbs.	Roots. lbs.	Efficiency.
28	7	0	126	– 10
31	0	7	126	– 9
37	7	0	150	– 7
45	10	0	100	– 5
59	7	0	120	– 1
85	0	17	48·4	– 1

Eight lots were fed on long fodder and concentrates, with minus efficiencies in six cases, namely: —

No.	Straw. lbs.	Hay. lbs.	Concentrates. lbs.	Efficiency.
15	0	14·63	6	+ 1
19	13·6	0	10·4	− 6
68	0	22	6	− 5
75	9·5	5	13	− 6
79	7	7	9	− 4
80	14·1	0	10	− 4
97	11	5·5	9·4	− 4
106	0	7·7	10·5	0

Two lots were fed on roots and concentrates, both with minus efficiencies, namely:—

No.	Roots. lbs.	Concentrates. lbs.	Efficiency.
70	131·11	4·6	− 2
81	127·03	7·72	− 3

It is obvious that such rations are generally inefficient, more especially when they contain large supplies of roots.

On running down the figures for the remaining rations, all of which contained the three ingredients, long fodder, roots, and concentrates, it will be seen that efficiency does not vary with the quantities of either long fodder or concentrates, for, among the rations falling to the right side of the upright line, the former run from 16 lbs. down to 8 lbs., and the latter from 10 lbs. down to 3 lbs. Generally the quantity of long fodder is smallest in the most inefficient rations; but the inefficiency is not due to this. The ingredient which clearly affects the efficiency of a ration and, at the same time, keeps down the consumption of long fodder, is the roots. Leaving aside the 6-cwt. and 7-cwt. groups, in which the variations are small, the most inefficient rations contained large quantities of roots, and, as the rations increased in efficiency, the quantities of roots generally declined.

If a rough opinion may be hazarded, which is all that may be done in the meantime, it is that the efficiency of a ration runs risk of being lowered when the roots in it are over 80 pounds. In Fjord's second experiment with cows, it was found that about 50 pounds of roots might be added to a usual ration of long fodder and concentrates, and the cows would consume the normal ration as before, plus the roots, and at the same time give two or three pounds more milk a day. Later experimenters found, however, that

the quantity of roots could not be increased much further without the efficiency of the whole ration being depressed. For this there are three, perhaps more, possible reasons: that the bulk of the whole ration gets beyond the manipulative capacity of the stomach, and that energy is lost, first, in heating up the water in the roots, and, second, in afterwards eliminating it from the system.

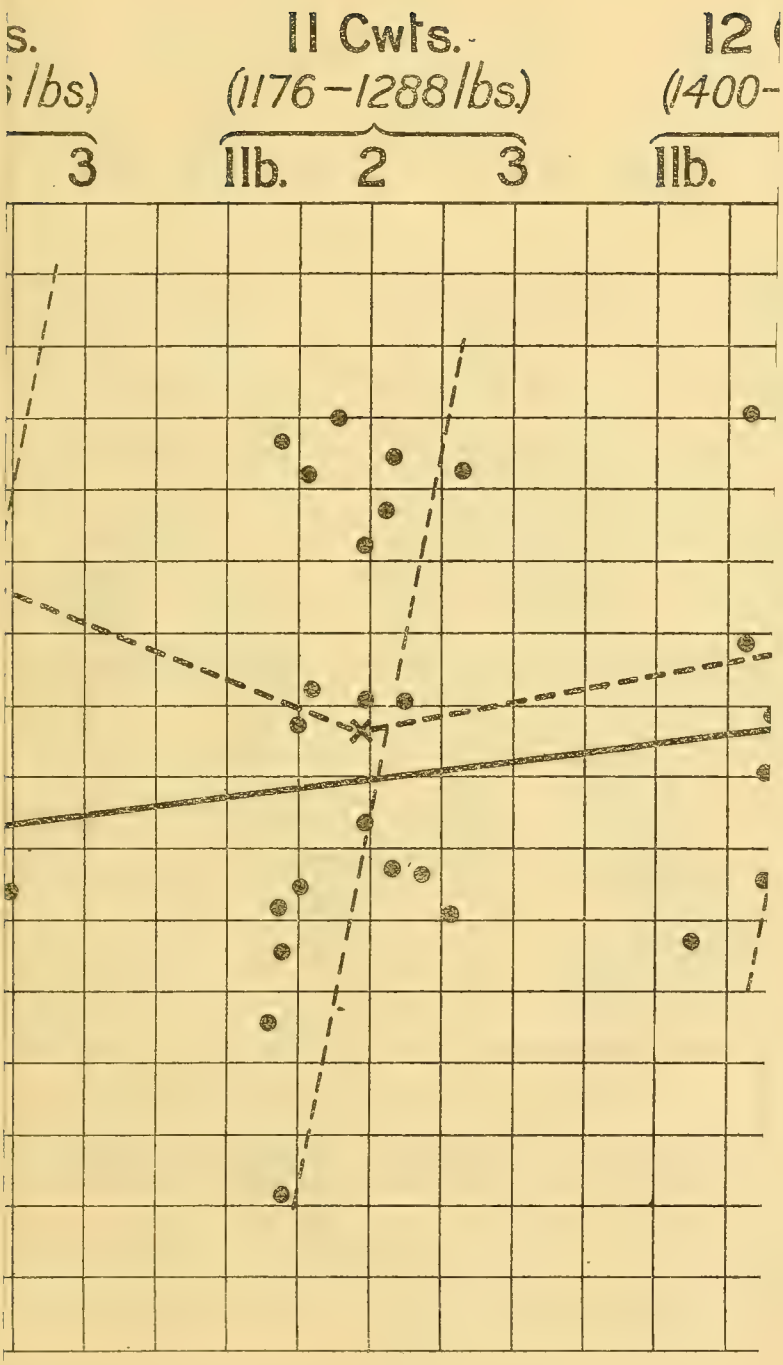
It will also be noticed, in the rations containing less than 80 pounds of roots, that the less efficient rations frequently contain straw alone, or more straw than hay, while the quantities of these two long fodders are as frequently reversed in the more efficient rations. It might be suggested, therefore, that a ration like the following might, with 9-cwt. cattle, be a starting-point from which to discover still more efficient rations:—

Oat straw,	4 lbs.,	1 food-unit.
Hay,	10 lbs.,	4 „
Mangels,	70 lbs.,	7 „
Concentrates,		4 „

The following are the figures, as taken from Professor Nils Hansson's "Utfodringslära," published in 1916, by which the various foods have been divided in order to reduce them to their equivalent in barley:—

Hay,	2·5[1]	Linseed cake,	·9
Oat straw,	4	Rape cake,	·95
Barley straw,	4	Gluten feed,	·95
Wheat straw,	5	Maize or Indian meal,	·95
Potatoes,	4	Beans,	1
Carrots,	8	Wheat,	1
Swedes,	9	Barley bran,	1·2
Mangels,	10	Oats,	1·2
Turnips,	12·5	Dried grains,	1·3
Linseed,	·6	Molasses,	1·3
Earthnut cake,	·8	Undecorticated cotton cake,	1·4
Sesame cake,	·8	Barley,	1
Decorticated cotton cake,	·85		

[1] In a few cases hay is called clover hay. The figure by which pure clover hay should be divided is 2·2, but as grass and clover hay is usually called clover hay, the figure 2·5 has been used in all cases.


s.
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3
11 Cwts.
(1176–1288 lbs.)
11lb. 2 3
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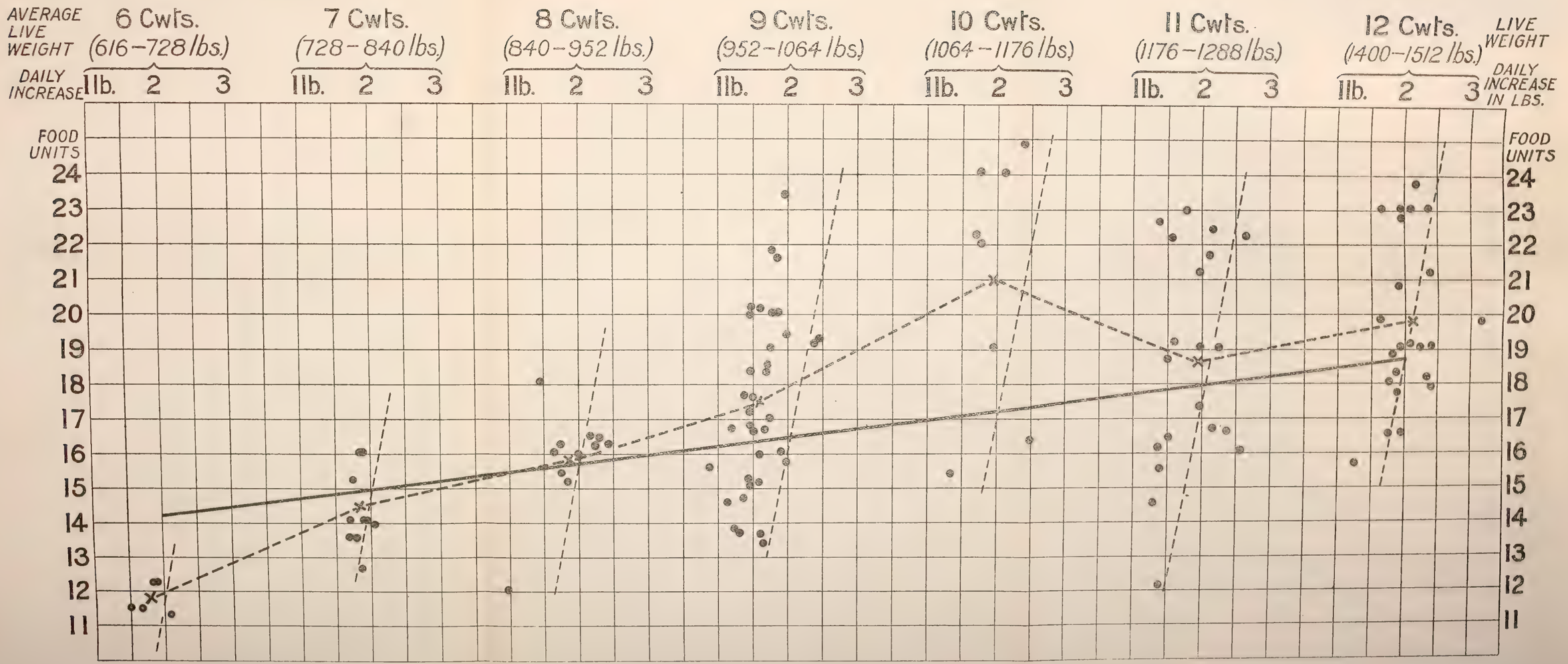
AVERAGE LIVE WEIGHT
DAILY INCREASE
6 Cwts. (616–728 lbs.)
7 Cwts. (728–840 lbs.)
8 Cwts. (840–952 lbs.)
9 Cwts. (952–1064 lbs.)
10 Cwts. (1064–1176 lbs.)
11 Cwts. (1176–1288 lbs.)
12 Cwts. (1400–1512 lbs.)
1lb. 2 3
LIVE WEIGHT DAILY INCREASE IN LBS.
FOOD UNITS
24
23
22
21
20
19
18
17
16
15
14
13
12
11

SCIENTIFIC PROCEEDINGS.

VOLUME XVI.

1. A Cryoscopic Method for the Estimation of Sucrose. By Henry H. Dixon, sc.d., f.r.s., and T. G. Mason, m.a., sc.b. (January, 1920.) 6*d*.
2. The Carboniferous Coast-Section at Malahide, Co. Dublin. By Louis B. Smyth, b.a., sc.b. (Plates I., II.) (February, 1920.) 1*s*.
3. The Application of the Food-Unit Method to the Fattening of Cattle. By James Wilson, m.a., b.sc. (Plates III., IV.) (February, 1920.) 1*s*.

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THE HOLOTHURIOIDEA OF THE COASTS OF IRELAND.

BY

ANNE L. MASSY.

Smithsonian Institution
MAR 5 1921
National Museum

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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Smithsonian Institution
MAR 5 1921
National Museum

IV.

THE HOLOTHURIOIDEA OF THE COASTS OF IRELAND.

By ANNE L. MASSY.

Read December 16, 1919. Published April 8, 1920.

About 25 species of this group are distributed round our shores and in the deep water off the west coast, and further research in the latter region will probably add to the number. Among the specimens taken by the naturalists of the Fisheries Branch of the Department of Agriculture and Technical Instruction for Ireland since the publication of Mr. Kemp's paper[1] the following are additions to the British and Irish area:—*Stichopus regalis* (Cuvier), *Mesothuria Verrilli* (Théel), and *Benthogone rosea*, Koehler. Four other species, *Bathyplotes Tizardi* (Théel), *Mesothuria lactea* (Théel), *Cucumaria Normani*, Pace, and *Pseudocucumis mixta*, Östergren, possess names new to the Irish fauna; but I believe they have been already found off our west coast, but were recorded under other names. *Mesothuria lactea*, *Mesothuria Verrilli*, and *Benthogone rosea* appear to be species of the warmer parts of the Atlantic, and probably reach their northern limit at about 52° N. latitude. *Stichopus regalis* occurs in the Mediterranean, and is known as far south as the Canaries, but has not until now been observed north of the Bay of Biscay. It has been recorded from Australia with a query by Semper; but as it is not a very deep water species, it would seem to be more likely that the Australian record refers to the nearly allied *Stichopus nigripunctatus*, Augustin, a Japanese species. *Bathyplotes Tizardi* is a deep water species, with a range extending in the Atlantic from 60° N. lat. to Senegal. It has also been recorded from Japan, and probably future investigation will show that, like *Laetmogone violacea*, Théel, it is an oceanic species of very wide distribution. *Pseudocucumis mixta* is known from western Europe, and seems to have been frequently confounded with *Phyllophorus pellucidus* and other species. Östergren, with regard to this confusion, has pointed out the importance of studying the calcareous collar in Holothurians, as species having much the same outward appearance, and apparently identical deposits, may possess collars of a totally different structure. The only British species which have not been observed on our coasts appear to be *Cucumaria frondosa* (Gunnerus) and *Labidoplax Buski*

[1] "Ann. Rep. Fish. Irel.," 1902-03, pt. ii, App. vi (1905).

(M'Intosh). The latter is a sub-Arctic species, which appears to reach its southern limit in Scottish waters. *C. frondosa* is widely known in Arctic waters, but has also been taken off the coast of Portugal [*Porcupine* Exp.], and in Florida and California. Although we do not, as in the east, make use of any of our Holothurians in the preparation of the far-famed soups, &c., known as Trepang and Bêche de Mer, yet, indirectly, they certainly are of use to us, since many records exist of their occurrence in the stomachs of some of our more important food fishes, e.g., the cod, haddock, and plaice (Forbes, 1841; Leslie and Herdman, 1881; and Östergren, 1902). I have to thank Mr. Nichols and Miss Stephens, of the National Museum, Dublin, and Mr. Deane, of the Belfast Museum, for much help in trying to trace the types of early records of more or less doubtful species, also for the loan of specimens for examination.

The following is a revised list of species of the coast of Ireland :—

Holothuria Forskahli, Delle Chiaje.
Stichopus tremulus (Gunnerus).
„ *regalis* (Cuvier).
Bathyplotes Tizardi (Théel).
Mesothuria intestinalis (Asc. & Rath.).
„ *Verrilli* (Théel).
„ *lactea* (Théel).
Laetmogone violacea, Théel.
Benthogone rosea, Koehler.
Cucumaria elongata, Düb. & Kor.
„ *lactea*, Forbes & Goodsir.
„ *Hyndmani* (Thomps.).
„ *hispida* (Barrett).
„ *Normani*, Pace.
„ *saxicola*, B. & R.
Thyone fusus (O. F. Müll.).
„ *raphanus*, Düb. & Kor.
Phyllophorus pellucidus (Flem.).
„ *Drummondi* (Thomps.).
Pseudocucumis mixta, Östergren.
Labidoplax digitata, Mont.
„ *digitata*, var. *profundicola*, Kemp.
„ *Thomsoni* (Herapath).
Leptosynapta inhaerens (O. F. Müll.).
Psolus phantapus (Struss.).
„ *Fabricii*, Düb. & Kor.

The following doubtful species has also been recorded from Ireland:—

Cucumaria Andrewsi (Farran), 1852.

Order ACTINOPODA.

Sub-order 1. **ASPIDOCHIROTAE.**

Family HOLOTHURIIDAE.

Holothuria Forskahli, Delle Chiaje, 1823.

Holothuria nigra, Gray, 1848.
„ *catanensis*, Grube, 1864.
Stichopus Selenkae, Th. Barrois, 1882.
Holothuria Forskalii, Marenzeller, 1893.

A. 94—Dredge, 8 fms. One, eight inches in length.
W. 36—Trawl, 16–22 fms. One.

Authentic records of this species show that it lives in many parts of the west of Ireland, from the Kenmare River to Donegal, from between tide-marks to a depth of 30 fms. (Nichols, 1903 and 1912; Kemp, 1905).

Distribution.—West Ireland and south-west England to Mediterranean.

Stichopus tremulus (Gunnerus), 1767.

Stichopus Richardi, Hér., 1896.
Holothuria ecalcarea, M. Sars, 1858.
„ *calcarea*, Jarzynsky (Wagner, 1885)

This species is widely distributed off the west coast of Ireland, and occurred in 76 of our hauls from 50° 14′ N. to 54° 7′ N. lat., by 10° 24′ W. to 14° 34′ W. long., at soundings of 72–710 fms. Two-thirds of these stations were in the southern half of the area. Of those stations where the depth was 200–700 fms., it was abundant in more than half. Where the depth was 200 fms. it was abundant in one third of the hauls. Where the depth was only 72–100 fms. it was abundant at one-eighth of the stations. A wide tract from 52° to 54° N. lat., by 11° to 14° W. long., with a depth of 91–208 fms., was explored by 15 hauls, and here the present species was the only Holothurian observed, dense populations being noted on four occasions. It was always associated with *Spatangus Raschi*, Loven, and sometimes with *Luidia Sarsi*, Düb. & Kor, and *Echinus acutus*, Lam^{k}. Between 54° and 55° N. lat. it shared the

deeper water with *Mesothuria intestinalis* (Asc. & Rath.), *Cucumaria hispida* (Barrett), and *Laetmogone violacea*, Théel. Nichols (1902, p. 245) enumerates 8 records of various expeditions off the west of Ireland (6 off the Kerry coast) at soundings of 70-500 fms.

Distribution.—Norway and Shetland to north coast of Spain, 45–672 fms. (Bell, 92A). 1476 fms. [*Porcupine* Exp., 1869].

Stichopus regalis (Cuvier), 1817.

Holothuria columnae, Cuvier, 1817.
„ *triquetra*, Delle Chiaje, 1828.

Five specimens, 75–155 mm. in length.

The above were trawled by the *Helga*, but unfortunately the label belonging to them has been lost.

The calcareous deposits in skin were compared with those of a specimen from the zoological station at Naples, now in the Irish National Museum.

Distribution.—Bay of Biscay, Canaries, Mediterranean, (?) Australia (Semper, 1868[1]).

Vertical Range.—Abundant between 55 and 98 fms. (Koehler, 1896); 58–224 fms. (Perrier, 1902).

Family SYNALLACTINAE.

Bathyplotes Tizardi (Théel).

Bathyplotes natans, Sladen, 1891.
Stichopus Tizardi, Théel, 1882; Bell, 1892; and Koehler, 1896.
Herpysidia (*Stichopus*) *Tizardi*, Perrier, 1898.

S.R. 331—Trawl, 610–680 fms. Twenty-one.
S.R. 336—Trawl, 673–720 fms. Five.
S.R. 500—Trawl, 623–666 fms. Two.

These specimens measure 75–110 mm. in length. About sixty other specimens (not preserved) were trawled in 10 hauls in the same area, namely, from 50° 30′ to 51° 45′ N. lat., and from 11° 20′ to 12° 30′ W. long., over soundings of 400–770 fms. The specimens referred by Sladen ('91, p. 702) to *Bathyplotes natans* (Sars) were taken within this area. I have been able to examine two of these specimens, which are deposited in the

[1] See note in preface.

Irish National Museum, and their spicula, though partly dissolved, and their external appearance prove them to be the same species which is here referred to *B. Tizardi*. It will be remembered that Bell (1892, A, p. 51) expressed much doubt as to the correctness of Sladen's identification. Östergren (1902, p. 6) is of opinion that up to the present *B. natans* has only been observed with certainty on the west coast of Norway from 60° to 69° N. latitude. The specimens from the three hauls given above, as well as those not preserved, were all entered in the log-books as "squashy red Holothurians." In alcohol they are cream colour above and deep buff on the ventral surface. Owing to their very slimy skin, they are frequently thickly covered with grey sponge spicula, fish scales, &c.; a mounted portion of the perisome of one specimen displayed (mixed up with its own deposits) a number of wheel-shaped deposits of *Benthogone rosea*, Koehler, which happened to be abundant in the same haul. The spicula, as in the description of the type, consist of a cross, or, more rarely, a star, with enlarged ends pierced with one or more holes. The enlarged ends are often connected so as to form an annular disc. As in *B. patagiatus*, Fisher (1907, p. 689), annular discs are very numerous on the ventral surface. Eight cross-beams are usually present in the spire of the tables of the papillae. These tables have the disc much reduced, and rarely annular, as far as examined. The tables of the pedicels have an annular disc, and a short spire of two cross-beams. They are further supported by slightly curved spinose rods and a terminal plate, which is sometimes split up into a few small jagged plates. As in *B. patagiatus* (*op. cit.*, pp. 688-9), C-shaped spicula are very abundant in the walls of the anus, and on the gonadial tubes, but appear to be absent from the outer integument. *B. bipartitus*, Hérouard (1912, p. 4), agrees with the present specimens in the absence of external C-shaped spicula, but it has pedicels along the entire median line of the ventral surface, whereas in our specimens this part is always defined by a deep groove, in which no pedicels were detected. *B. reptans* (Perrier, 1902, p. 352) resembles our examples in the red colour of body and shape of deposits, but it has far more dorsal papillae. Koehler describes the colour of *B. Tizardi* as grey, and Perrier supposes that this description refers to the living animal, since Koehler's other descriptions were based on such. Probably variations in colour occur according to the conditions of environment, and a pale-coloured form, coated with grey ooze and pearly fish scales, could only be described as grey.

Distribution.—Färöe Channel, 530–555 fms. (Théel, 1882). Bay of Biscay, 355–710 fms. (Koehler, 1896). West coast of Morocco, Sahara, and Senegal (Perrier, 1902). South Norway (Östergren, 1902). Japan (Ohshima, 1915).

Mesothuria intestinalis (Asc. & Rath.).

Holothuria intestinalis, Asc. & Rath., 1767.
Thyonidium scabrum, Sars, 1868.

S.R. 222—Trawl, 293 fms. One.
S.R. 327—Trawl, 550 fms. Sixteen.
S.R. 493—Trawl, 533–570 fms. Two.
S.R. 1690—Trawl, 584 fms. One.

Previous Irish records.—Off S.-W. Ireland, 345–750 fms. (Sladen, 1891); off Eagle Island, Co. Mayo, 70 fms.; and off S.-W. Ireland, 190 fms. (Kemp, 1905).

Many writers hold the view that *M. Verrilli* (Théel) is a variety of the present species frequenting very deep water. R. Perrier (1902, pp. 309–12) and Östergren (1902, pp. 6–7) have shown that they are distinct. The deposits in the perisome of both species are very much alike, and both may be found in the same area, and here the similarity, other than generic, seems to end. Specimens from our hauls, in alcohol, are absolutely unlike each other in appearance. *M. intestinalis* is invariably of a uniform cylindrical shape, so that if the tentacles are withdrawn it is difficult to recognize at which end the head is situated. The body is pale brown (exceptionally almost white), with a much-wrinkled surface, usually coated with débris (such as sponge spicula and echinoderm spines), and the pedicels are distributed on the anterior trivium as elsewhere. *M. Verrilli*, on the contrary, has hardly any pedicels on the anterior part of the trivium, which is somewhat flat, and the pedicels everywhere are much finer. In a specimen measuring 300 mm. in length and 80 mm. in diameter the pedicels are usually only about half the thickness of those in an example of *M. intestinalis* measuring 90 mm. in length. As Perrier (*op. cit.*, p. 310) has remarked, the pedicels, instead of containing tables of similar size to those of the perisome, as in *M. intestinalis*, are too small to contain other than minute, somewhat rudimentary tables, the terminal plate being also much smaller, and with more jagged edges. The species is further characterized by the clean surface and white colour of the body, which is usually much broader in the centre and constricted at the extremities, and the latter are frequently directed ventralwards.

Although the two species were not taken together in our hauls, there is evidence to show that both occur off south-west Kerry from about 50° to 52° N. lat. and 11° to 12° W. long. *M. Verrilli* was only taken between the 500 and 1000-fm. line. There are 4 records of *M. intestinalis* within this area, against 5 records at about the 200-fm. line. Further north

(between 53° and 54° 33′ N. Lat.) *M. Verrilli* was not observed, and there were only 3 takes of *M. intestinalis.*

Distribution.—Murman coast, Norway, Kattegat, Scotland and Ireland, Bay of Biscay to south of Canaries.

Vertical Range.—164–784 fms.

Mesothuria Verrilli (Théel), 1885.

Mesothuria Verrilli, Perrier, 1899.
Allantis intestinalis, Asc. & Rath., var. *Verrilli*, Hérouard, 1899.

S.R. 336—Trawl, 673–720 fms. Four.
S.R. 477—Trawl, 707–710 fms. One.
S.R. 494—Trawl, 550–570 fms. Three.
S.R. 497—Trawl, 775–795 fms. Two.
S.R. 593—Trawl, 670–770 fms. One.
S.R. 944—Trawl, 982 fms. Two.

Some of the differences between this species and *M. intestinalis*, as taken in our hauls, have already been noted (p. 42).

Distribution.—Atlantic from 12° to about 50° N. lat. (Östergren, 1902).

Vertical Range.—300–2277 fms. (Perrier, 1902).

Mesothuria lactea (Théel).

Holothuria lactea, Théel, 1885.
? *Holothuria aspera*, Bell, 1889.
Synallactes lactea, Hérouard, 1896.
Mesothuria lactea, Östergren, 1896.
Zygothuria lactea, R. Perrier, 1899.

S.R. 336—Trawl, 673–720 fms. Nine.
S.R. 944—Trawl, 982 fms. Twenty-seven.

The specimens of the first haul measured 60–77 mm. 14 specimens preserved from the other haul measured 45–100 mm. Like Hérouard (1902, p. 22), I have been unable to discover any appendages except a single row on each of the latero-ventral ambulacra. The skin is, however, often much wrinkled or abraded. Hérouard (*op. cit.*, p. 21) found this species in great abundance in the Azores region, at soundings of 656–1093 fms. Bell's brief description (1889, p. 445) of *Holothuria aspera*, taken in the *Flying Fox* Exp. off S.-W. Ireland, at soundings of 1000 fms., seems to refer to a creature with many points of resemblance to the present species, namely, colour, size, skin, wrinkled above and smooth below, with "a single row of not closely

packed podia" on each side, and, lastly, the spicula figured are very like the beautiful wide-meshed disks of *M. lactea*, if the deposits examined had the outer rings of the tables broken away or not developed. Amongst the specimens of *M. lactea* from station S.R. 944 a portion of the perisome exhibits disks of this description with only 6 spokes and a central hole; and none of the table spires appears in this particular part, although abundant in the remaining portion of the mount. I have had no opportunity of examining the type of *H. aspera* which is preserved in the British Museum.

Distribution.—North Atlantic, from Bay of Biscay to Azores (Koehler, 1896, and Hérouard, 1902). Pacific (Théel, 1885). Indian Archipelago (Sluiter, 1901).

Vertical Range.—498–1235 fms. (Sluiter, 1901, and Perrier, 1902).

Family ELASIPODIDAE.

Laetmogone violacea, Théel, 1879.

Cryodora spongiosa, Théel, 1882.
Laetmogone spongiosa, Théel, 1882.
„ *Jourdaini*, Petit, 1885.
„ *Brongniarti*, E. Perrier, 1886.

About 2000 examples of this species are recorded in the log-books. They occurred in 36 hauls at soundings of 250–778 fms., and in the lat. 50° 21′ to 52° N., and between 11° and 12° 54′ W. long. Of the 2 previous Irish records, that of the *Flying Falcon* (Sladen, 1891) was withinthese limits, but the *Helga* station was much further north at 53° 58′ N., 12° 26′ W. (Kemp, 1905). Examples from 3 stations (S.R. 327, 333, and 336) were preserved, and measured 12–140 mm. The hauls extended over a period of 9 years, and young ones were noted in 4 May and 10 August–September hauls. From year to year, in winter and summer hauls, it was observed in abundance only at various points at about the 500-fathom line. As the specimens which were not preserved were not microscopically examined, it is possible that some of them may have been referable to *Laetmogone Wyville-Thomsoni*, Théel, which was taken by the *Caudan* Expedition in the Bay of Biscay in 6 hauls, and which Koehler (1896, p. 118) considers to be one of the commonest Elasipods in the North Atlantic.

Distribution.—Färöe Channel, Bay of Biscay to Senegal and Azores, Maldives, Andamans, Moluccas, Japan, off Sydney. The greatest depth recorded seems to be that of the *Challenger* Exp. at 950 fms.

Benthogone rosea, Koehler, 1896.

S.R. 336—Trawl, 673–720 fms. One hundred and five.
S.R. 593—Trawl, 670–770 fms. Many.
S.R. 944—Trawl, 982 fms. Forty-four.

The samples preserved average 120 mm. in length. The ventral appendages are purple in alcohol, and this colour suffuses the otherwise white surface. The integument is 4–5 mm. thick, and, as in the type, is closely sprinkled with red-brown dots on the inner surface, with rows of brown markings on the 5 muscle bands. The deposits agree with those of the type. Although 4 is the usual number of perforations in the centre of a wheel, 3 and 5 are of common occurrence.

Distribution.—Bay of Biscay, numerous examples (Koehler, 1896). Coast of Africa to Senegal, Canaries, only a few in each haul (Perrier, 1902).

Vertical Range.—603–1289 fms.

Sub-order 2. **DENDROCHIROTAE.**

Family CUCUMARIIDAE.

Cucumaria elongata, Düb. & Kor., 1844.

Cucumaria fusiformis, Forbes & Goodsir.
„ *pentactes*, Müller, 1788.

This has been taken by us on 9 occasions, at all seasons, on the east, west, and south coasts at depths of 2–37½ fms. It was usually observed in small numbers, but was abundant in autumn off Dundrum Bay, Co. Down, and Mine Head, Co. Waterford. It has been previously recorded from the north and east coasts under *Cucumaria fusiformis* (F. & G.), and from the south and west coasts under this name, and also as *Cucumaria pentactes* (Müll.). Théel (1885, p. 106) records it from 53° 23′ N., 13° 29′ W., at 85 fms. [*Porcupine* Exp.]. Figures of this species have been given by Kemp (1905, pl. 35, fig. 1) and Orton (1914, p. 230). A specimen measuring 70 mm. in length, and taken in the month of September, contained *ca.* 240 gonadial tubes. They were narrow and unforked, and averaged 15 mm. in length.

Distribution.—West coast of Scandinavia to Mediterranean (Théel, 1885). Plymouth (Orton, 1914).

Cucumaria Hyndmani (Thomps.), 1840.

We have dredged this species on 6 occasions in St. George's Channel, and also in Clew Bay and Killary Bay, at soundings 5–275 fms. It was observed in abundance in the latter inlet by Forbes (1841), and there are records of its

occurrence at Roundstone, Co. Galway (Thompson, 1856), off Dursey Head, Co. Cork (Sladen, 1891), and off the west of Ireland (*Argo* Cruise). A specimen in the Irish National Museum, measuring 20 mm. in length, was taken on the west coast of Ireland by the Royal Dublin Society in 1896, at soundings of 500 fms. The type specimen was dredged in Belfast Bay, and its presence in the Irish Sea has since been noted by Kinahan (1861) in Dublin Bay, and by Bell (1892) at Liverpool. A specimen of 37 mm. in length, captured in August, contained *ca.* 55 gonadial tubes, a few of which were bifurcated near the extremity. The tubes average 20 mm. in length, and ·50 mm. in diameter. They are about twice as wide as those of *C. elongata* and *C. Normani*, as far as examined, from specimens in our hauls.

Distribution.—West coast of Scandinavia south of the Arctic Circle to Mediterranean (Théel, 1885). West of Scotland, 420–630 fms. (*Porcupine* Exp.).

Cucumaria Andrewsi (Farran), 1852.

Clonea, Dungarvan, two specimens.

These specimens do not appear to be extant, and it seems best to let the name drop altogether, as the description is too incomplete. "Nothing can be said about this species except that it is certainly a *Cucumaria*; a leading ground for regarding it as new was the canary colour of the tentacles." (Bell, 1892A, p. 41.)

Cucumaria lactea (Forbes & Goodsir), 1839.

Holothuria brunnea, Thompson, 1840.
Ocnus lacteus, Forbes, 1841.
„ *brunneus*, Forbes, 1841.
Cucumaria lactea, Düb. & Kor.
„ *brunnea*, Hérouard, 1889.

From the evidence of many of our hauls, and from records of former observers (Nichols, 1903), it is apparent that this species is distributed on both the east and west coasts of Ireland, where we have taken it from between tide-marks to a depth of 52 fms. The latter soundings were made 10 miles east of Baily Light, Co. Dublin. Our east coast specimens, and an example from Dalkey, collected by the late Mr. Colgan, and presented to the Irish National Museum, belong to the brown form, but both white and brown examples occurred in the west coast hauls.

The spicula of the perisome are very much alike in this species and *C. Normani*. Orton (1914, p. 228) has shown that the present species belongs to the group having only a few tubes in the gonad; but if the specimen is

too young to show this character, the brown form may be distinguished from the young of *C. Normani* by the more slender body, and by the campanulate spicula having more holes, and being in want of a true rim (Théel, 1885, p. 102), also by the absence of the 3-legged spicula common in *C. Normani*.

Our smallest specimen of *C. lactea*, with gonad developed, measures 11 mm., and has 6 tubes of about 2 mm. in length.

Specimens of 18–35 mm. have 9–20 short thick tubes. It was observed that the smaller of the specimens examined had 1 polian vessel, and the larger 2 vessels.

This species seems to come next to *C. saxicola* in being one of the commonest of the Cucumarians on our coast. Two-thirds of the older specimens from our gatherings were shore-collected.

Distribution.—British seas and west Norway, 0–50 fms.

Cucumaria hispida (Barrett), 1857.

Echinocumis typica, M. Sars, 1858.

S.R. 497—Trawl, 775–795 fms. One.
S.R. 752—Trawl, 523–595 fms. Eight.
S.R. 851—Trawl, *ca.* 900 fms. (?) One.
S.R. 1844—Mosquito-net tow-net on trawl, 417–565 fms. Four.

Previous Irish records—54° 1′ N., 12° 14′ W., 422 fms.; 50° 1′ N., 12° 26′ W., 1207 fms. (*Porcupine* Exp., 1869).

The above measure 6–20 mm. in length. The example to which a query is affixed was unfortunately preserved in formalin, and the spicula have in consequence dissolved away.

The other specimens resemble those figured by Bell (1892A, pl. 4, fig. 1), except that the plates usually have a marginal row of much smaller perforations. Nothing approaching to the var. *abyssalis* (Koehler, 1896, p. 119, pl. 2, fig. 22) was observed. Portions of skin from a specimen from station S.R. 752 have plates measuring about 556μ by 657μ, and containing about 83 smooth-edged holes, of which the central group are much the largest. The spires measure about 267 to 333μ by 55μ at the widest part. They are slightly spinous, and have oblong perforations.

Distribution.—Arctic Sea to Bay of Biscay, 40–550 fms. (Bell, 1892 A).

Cucumaria Normani, Pace, 1904.

Pace (1904–7) and, subsequently, Orton (1914) have definitely cleared away all mystery from the characters of this and the next species, and have shown that it is better to drop altogether the names of *Holothuria Montagui*, Flem.,

and *Holothuria pentactes*, Müll., as the descriptions of these animals by the earlier naturalists are insufficient to enable us to identify them. Much, however, remains to be done before the geographical distribution of the present species and *C. saxicola*, B. & R., can be definitely established. Orton (*op. cit.*, p. 225) observes that there is little doubt that both *C. Normani* and *C. saxicola* "occur on the Continent, but at present pass under other names." As yet we have met with *C. Normani* only on the west coast. A few specimens occurred in 3 shore collections, and it was dredged on 2 occasions at 5½–11 fms. in the area between Clew Bay and Galway Bay. Some of these, and a specimen from Westport Bay in the Irish National Museum, have been already recorded under *C. Montagui* (Nichols, 1912; Farran, 1915). The last-mentioned specimen measured 28 mm. in length, and contained *ca.* 180 tubes in the gonad. The other specimens measured 15–48 mm. in length. All are brown in alcohol. A specimen of 15 mm. had 120 straw-coloured tubes in gonad, while one of 40 mm. had only *ca.* 80 tubes, and one of 35 mm. had *ca.* 146.

Distribution.—Plymouth. Polperro, Cornwall.

Cucumaria saxicola, B. & R., 1871.

There is no doubt that this species was known to the earlier naturalists, but its characters were in part mixed up with those of other species. The first complete description was given by Brady and Robertson (1871, pp. 690–1) from specimens taken by them in holes of limestone boulders between tide-marks, Westport Bay, Co. Mayo, and Birterbuy Bay, Co. Galway.

Between 1899 and 1916 we have taken it 34 times,[1] sometimes abundantly, at various parts of the west coast, from Lough Hyne, Co. Cork, to Lough Swilly, Co. Donegal. Fully two-thirds of the gatherings were made on shore, but it was also dredged at soundings of 1–25 fms. Although we did not meet with it in any of our east-coast hauls, it will probably be found there. I have seen a white Cucumarian of 12 mm. in the Irish National Museum, collected at Howth by Miss Stephens, which, in external appearance, is very like this species, but, unfortunately, the spicula were dissolved. A specimen of *C. saxicola* was taken in Lough Swilly, in 1900, by Dr. C. B. Ball, and is now in the Irish National Museum. Mr. Southern collected 3 examples at Portmon Bay, Portstewart, Co. Londonderry. The specimens from our gatherings measured 4–30 mm. Specimens from 16–18 mm. possessed 5 gonadial tubes (in the specimen of 18 mm. one tube measured 15 mm.), and specimens from 25 to 30 mm. had 5 to 8 tubes. In

[1] Some of the specimens have been already recorded (Nichols, 1912, and Farran, 1915).

one September haul the tubes were observed to be full, but usually, as far as examined, they were empty in August and September.

Distribution.—Plymouth. Probably distributed on the Continent, but passing under another name (Orton, 1914).

Thyone fusus (O. F. Müll.), 1788.
„ *fusus*, Düb. & Kor, 1844.
„ *papillosa*, Forbes, 1841.

Nichols (1903, p. 243) enumerates 5 records of the occurrence of this species on the west coast of Ireland, and 7 records in the Irish Sea, from Larne to Dublin Bay. We have trawled a specimen off Chicken Rock, I.O.M., and another example, apparently referable here, but of which the spicula had dissolved, was taken in St. George's Channel. From 51° 28′ N. to Clew Bay we trawled it in 18 hauls at soundings of 2–342 fms. Usually only 1 or 2 specimens occurred, but 5 were observed on one occasion (in 22 fms., on gravel and stones, off Dingle Lt. Ho.).

In size our specimens varied from 6–105 mm. A number of specimens from 17 to 78 mm. in length were found to possess 1 simple polian vessel, sometimes dilated in the middle. The smallest specimen with gonad developed measured 8 mm., and contained 8 gonadial tubes. A specimen of 17 mm. possessed 50 tubes, somewhat welded together. The tubes are very fine and narrow.

A specimen of 52 mm. contained about 650 tubes of about 15 mm. in length. An example of 78 mm., with collar of 23 mm., taken by Mr. Nichols in Bantry Bay, and now in the Irish National Museum, contained about 200 tubes, measuring about 25 mm., and a polian vessel of about 14 mm.

Distribution.—Lofoten to British Isles, France, Mediterranean.

Thyone raphanus, Düb. & Kor., 1844.

This species has previously been recorded only from our south-west coast (Nichols, 1903). We have taken it twice in the Irish Sea, namely, off Black Head, Co. Antrim, and off Chicken Rock, I.O.M., and 8 specimens occurred in two hauls off Co. Waterford. We also obtained it in Dingle Bay and Bantry Bay. Our specimens were trawled at soundings of 16½–45 fms. Once the bottom was muddy sand, and the other hauls occurred on fine or coarse sand, or on a bottom of gravel and shells. Some specimens examined measured 10–23 mm. All had an unforked polian vessel, dilated in one or more places. Specimens of 15–16 mm. possessed 60–90 gonadial tubes, and one of 23 mm. had at least 120 tubes. The sexual products were more

advanced in this specimen, which was taken in an August haul. The others examined were captured in them onths of May and August. Orton, (1914, pp. 232–4) has given recent notes and figures of this species from Plymouth specimens.

Distribution.—British and Norwegian seas, Mediterranean.

Phyllophorus pellucidus (Flem.).

Holothuria pellucida, Flem., 1828.
Cucumaria hyalina, Forbes, 1841.
Thyonidium pellucidum, Düb. & Kor., 1846.
Phyll. pellucidus, Bell, 1892.

A specimen in the Irish National Museum, taken off S.-W. Ireland, in 50 fms., by the R.I.A. Exp. (Sladen, 1891), measures 74 mm. in length, and has a collar of 6 mm., with no prolongations. The tentacles are 19 in number. The gonad contains 60 tubes of 3–16 mm. A few are bifurcated, and about half are so branched as to equal about 10 simple tubes. There is one long, narrow polian vessel. I have not been able to see the specimen from Strangford Lough referred to *C. hyalina* (Hyndman and Thomps. f. Dickie, 1858), and, as noted (p. 52), the other Irish records appear to be referable to *Ps. mixta.*

Distribution.—Arctic seas, British Islands, and West Indies.

Phyllophorus Drummondi (Thomps.).

Cucumaria Drummondii, Thomps., 1856.
Thyone Portlockii, Forbes, 1841.
Thyonidium commune, Düb. & Kor., 1844, and Théel, 1885.
Phyllophorus drummondii, pro parte, Bell, 1892.
(non *Thyonidium dübeni*, Norman, nec.
Semperia drummondi, Hérouard, 1889.

We have not taken any specimens of the above in our investigations. The records given by Nichols (1903, p. 244), on account of the insufficient descriptions of the old writers, cannot be relied upon unless the specimens are extant. Mr. Nichols has courteously allowed me to examine the only two examples in the Irish National Museum. These specimens measure 70–92 mm. in length, less tentacles. Each has at some previous time been more or less cut open for investigation, so that it is possible that they may be type and co-type specimens of Forbes. The smallest specimen is labelled "*Phyllophorus drummondi*, Thomps. = *Thyone portlocki*, Forbes, Belfast Bay, Ord. Surv. Coll." The type of Forbes is described as measuring

5 inches when alive, and the specimen is now only half that size. The larger specimen, labelled "*Phyllophorus drummondi* = *Cucumaria cucumis*, Co. Antrim, Ord. Surv. Coll.," is now nearly $3\frac{3}{4}$ inches in length. Drummond described the type-specimen as being nearly as large as a middle-sized lemon the day it was captured, and next day "two inches long, and contracting itself slowly in many places." Thompson gives the length as 10 inches. As both these specimens come from the historic locality, and were taken during the Ordnance Survey investigations of Capt. Portlock, probably at least 80 years ago (Forbes, 1841, p. 238), it seems very probable that they were examined by those early naturalists who laid the foundation of our present knowledge of the group. The largest specimen has 9 outer, many-branched, white tentacles, the largest of which measures 25 mm. Seven very small tentacles, also white, form an inner ring. The other specimen has 18 tentacles (9 outer and 9 inner), measuring from 4–24 mm., and all more or less tinged with purple. The tentacles are, however, retracted, so that they have not been exposed to the light, which has, perhaps, bleached the extended tentacles of the larger specimen. In both examples no deposits were detected, even in the anterior portion of the perisome, other than the domed terminal plates in the podia. These measure *ca.* 599μ in diameter, and have a slightly serrated margin, and contain an immense number of small perforations, the largest of which measure *ca.* 22μ in diameter. These holes are frequently strengthened by transverse bands, and the largest may be either at the summit or margin. The deposits of the tentacles consist of densely packed plates, varying greatly in size and shape, and all containing a number of perforations. A typical plate measures 198μ by 121μ, and contains *ca.* 25 perforations, the largest of which measures *ca.* 20μ. Some plates are small, and contain but 6 perforations. A few rude tables are also present in the tentacles of both, and are apparently built up of 3 or 4 rods and 1 transverse beam, and possess a central and 7 peripheral holes, and measure *ca.* 77μ by 88μ. Both specimens are much contracted. The ambulacra are defined by grooves and by the presence of a large number of podia. The latter are also present on the interambulacra, but are there frequently separated by relatively wide spaces. Both specimens have a rather soft collar, measuring 15 mm. in height, and moderately excavated, but showing no trace of the prolongations present in *Ps. mixta*, Öst. It is the type of collar of *Ph. pellucidus* (Flem.). Each specimen agrees with the other in having 3 polian vessels, measuring 15–20 mm., and also in having lost both gonad and intestine. Östergren (1906, p. 18) thought it was possible that his *Ps. mixta* might prove to be Forbes' *C. Drummondi* if the latter was found to possess 20 tentacles. The shape of the collar is, however, totally

different from *Ps. mixta*. The species seems to be clearly distinguished from *Ph. pellucidus* by the absence of deposits in the perisome, by the collar, which is higher in proportion to the size of the animal, and by the very differently formed deposits of the tentacles. Also the present species is white, and *Ph. pellucidus* brown, in alcohol.

It has been suggested that the absence of deposits in the perisome may be due to age, as in *C. Hyndmani* (Thomps.) the deposits are frequently absent in large specimens. With regard to this it may be noted that *Ph. pellucidus* of 74 mm. has tables densely distributed in the perisome, while *Ph. Drummondi* of 70 mm. has no deposits.

Probably Östergren (*ib.*, p. 21) is right in considering that Bell may have had some specimens of *Ps. mixta* amongst his material when describing *Ph. Drummondi*. His figure 4 (1892 A) of Pl. V is much more like the richly perforated tables present in the perisome of *Ph. pellucidus* than those in the tentacles of the specimens under consideration. I have hesitated to include *Cucumaria communis* (Forbes) in the synonymy, as his figure (1841, p. 217), represents such a different-looking animal.

Distribution.—Scandinavian coast, from the Sound to Lofoten. British Isles (Théel, '85).

Pseudocucumis mixta, Östergren.

? *Holothuria neillii*, Flem., 1828.

? *Thyonidium commune*, Norman, 1869 (non *Cucumaria communis* Forbes; nec *Thyonidium commune*, Düb. & Kor.).

? *Phyllophorus drummondii*, pro parte, Bell, 1892.

Pseudocucumis mixta, Östergren, 1898.

„ *cuenoti*, Koeh. & Van., 1905.

S.R. 163—Dredge, 37 fms. ? One.

W. 210—Dredge, 21 fms. Two and two portions.

W. 216—Dredge, 18 fms. One.

This species, as regards external appearance and deposits, closely resembles *Phyllophorus pellucidus* (Flem.), to which species examples from the two last-mentioned hauls, and two specimens in the Irish National Museum from Kilkieran Bay, Co Galway, collected by A. G. More, have been already referred (Nichols, 1912). Through the kindness of Mr. Nichols, I was able to compare these with an example of *P. pellucidus*, also in the Dublin Museum, taken by the R.I.A. Exp. (Sladen, 1891).

The following differences may be noted :—

Ps. mixta—Posterior end of body narrow; podia only on ambulacra; colour in alcohol creamy white; tentacular spicula perforated; collar with prolongations of bead-like segments.

Phyll. pellucidus—Posterior end of body not narrowed; podia scattered; colour in alcohol brown; tentacular spicula without perforations, and armed with spikes; collar short, without prolongations.

One of our specimens of *Ps. mixta* measures 30 mm. in length, and has a collar of 6 mm., and one long simple polian vessel, with a dilation near the anterior portion, and another at the distal end. 15 small white oblong "buds," arranged in a row on wall of mesentery, appear to be gonadial tubes at an early stage of development. There are 20 tentacles, some of which are larger than the rest. Another specimen measures 53 mm. in length, and has a collar of 12 mm. There are at least 13 tubes in the gonad, mostly bifurcated, and some divided into 3. Of the Kilkieran specimens, one measures 34 mm. in length, and has a collar of 8 mm. There are 10 small inner tentacles, and 10 long outer ones. The gonad contains *ca.* 76 tubes of 3–4 mm. in length; about 32 of these are bifurcated near the base, and a very few have 3 branches. The narrow simple polian vessel measures 11 mm. in length. The other specimen measures 23 mm. in length, and has 19 large and small tentacles. The gonad contains 6 tubes, of which 5 are bifurcated. The collar is 5 mm. in length, and shaped liked the others, i.e., with forked, radial-beaded prolongations, and unbifurcated inter-radial pieces. The polian vessel measures 7 mm.

Östergren (1906, p. 8, figs. 1–3) gives figures of the calcareous collar in *Ps. mixta*. He considers the species to be of southern origin, reaching western Europe with the warm currents of the Gulf Stream.

Distribution.—Arcachon to western Norway and Färöes (Östergren, 1906).

Psolus Fabricii (Düb. & Kor.), 1844.

Cuvieria fabricii, Düb. & Kor.

Two hauls made in different years at 51° 20′ N., 11° 35′ W., at soundings of 406–460 fms., proved that this species lives in abundance in the deep water off south-west Ireland. 17 specimens were also taken off Eagle Island, Co. Mayo, in 2 hauls, at soundings of 350–388 fms. (Kemp, 1905, p. 185). In our specimens, as far as examined, the deposits of the foot-sole closely resemble Bell's illustration (1892A, pl. 6, fig. 2). The podia are supported by terminal discs, with many perforations, and also by irregular-shaped plates, with 21 holes or less, and curved perforated rods. The sexes can be distinguished through the thin foot-sole by the gonad, which consists either of a twisted skein of narrow white tubes (found to contain long dark masses when examined microscopically), or a yellowish bunch of about 24 short thick tubes filled with spherical granules. One large globular polian vessel

is present. Some of the specimens were preserved in formalin, or in a mixture of formalin and alcohol. Their appearance was so different from that of the specimens preserved in alcohol only that they seemed to belong to another species. They were limpet-shaped and of a pinkish hue, with scales, smooth to the touch and eye. The specimens in alcohol were of a dirty brownish white, and had coarse overlapping scales, and the body was strongly compressed. These differences, however, were but superficial, and in every detail as to size and shape of the scales in the different parts of the body, in the shape of collar and form of deposits, all the specimens were in intimate agreement.

Distribution.—Circumpolar, extending as far south as Massachusetts Bay; Shetland; Japan; 5–148 fms. (Bell, 1892A).

Psolus phantapus (Struss), 1765.

This species has been recorded from Bangor, Co. Down (Thomps., 1856), and from north-east Ireland (Belfast, N.F.C. Guide), but no specimens appear to be extant.

Distribution.—Arctic seas to British Islands, and North Sea; New England.

Psolus sp.

A few young specimens occurred in 5 hauls along the west of Ireland at soundings of 250–560 fms. Bell (1892) has also recorded 3 young specimens from off Co. Mayo.

Order 2. PARACTINOPODA.

Family SYNAPTINAE.

Labidoplax digitata (Mont.), 1815.

Synapta digitata, Bell, 1892.

W. 141—Dredge, 37 fms. One, var. *profundicola*, Kemp.
S.R. 1176—Naturalists' dredge, 100 fms. One, var. *profundicola*.
S.R. 1391—Dredge, 149 fms. One, var. *profundicola*.
W. 262—Dredge, 6–7 fms. One.
S. 369—Trawl, 12½–13 fms. One.

Previous Irish records.—Near Carrickfergus Castle (Thomps., 1856); Counties Donegal and Galway, R.D.S. Fishing Surv., 1890 (Bell, 1892); Dingle Bay, 36 fms. (Beaumont, 1900); Ballynakill and Bofin Harbours, and off Slyne Head, 12 fms., var. *profundicola* (Kemp, 1905); Clare Island, 11–19 fms., *Helga* (Nichols, 1912).

Thompson regarded *L. digitata* from Carrickfergus as intermediate between that species and *L. inhaerens*, while Herapath recognized in it the type of *L. Thomsoni* (p. 56). Kemp (1905, p. 177) found this species to be much less common on the west coast of Ireland than *Leptosynapta inhaerens* (O. F. Müll.). It would seem from the above, however, to be distributed round much of our coast. As regards var. *profundicola*, no giant anchors were observed in any of the specimens, and, as in the typical *L. digitata* from shallow water, the anchors and plates are shorter in the anterior region: thus, in the type specimen of var. *profundicola*, an anchor in the anterior portion measures 150μ in length, and 124μ across the flukes. Another anchor measures 190μ in length, and 124μ across flukes. A plate measures 165μ by 132μ. The posterior end shows anchors measuring from 242-313μ. The plates are much narrower at the free end, and are a little, or much, shorter than the anchor, which may extend *ca.* 60μ beyond plate. There is no trace of a secondary network in any of the plates; and all the specimens in which tentacles are present agree with the shallow water examples in having 12 tentacles with sensory buds. The purple colour characterizing the var. *profundicola* seems to be very constant, and is still present in specimens which have been preserved 6-14 years in alcohol. An exception to this occurs in the specimen from station S.R. 1176, which is recorded in the log as "deep purple, almost black," and is now sand colour, although it has only been 7 years in alcohol. The plates were not quite like those usually present in the variety, and seemed to be intermediate in shape and strength between the broad solid plates of the shallow water form and the delicate, abruptly narrowed plate of var. *profundicola*. Plates of 154μ and 176μ in length measured 124μ in width. Another plate of 126μ measured 132μ in width. They usually possessed 6 or 7 large holes, with small ones disposed more or less all round them. A long, narrow perforation and some very small round ones were present in the handle. The anchors measured from 190 to *ca.* 300μ in length, the shaft being twice as long as the breadth across flukes. No giant anchors were observed. In the specimens from shallow water, a Ballynakill example had anchors measuring *ca.* 764μ by 350μ across flukes with plates of 385μ. The small anchors of the anterior region measure 143 to 154μ in length; and the plate is but little longer than broad, the length, including handle, being 166μ by 132μ in breadth. The example from Valencia Harbour shows giant anchors of 816μ by 378μ across flukes. A plate measured 599μ by 330μ. The inside of this specimen is missing; but a ring of skin taken from the thicker, and presumably anterior end, shows anchors of 165 to 302μ. The specimen from the east coast had lost its tentacles, so that it cannot be ascertained if

sensory buds were present. The plates had dissolved away before examination; but 4 anchors measuring from 165 to 220μ measured 132μ across the flukes. No giant anchors were seen. The specimens from Clare Island were in good condition, and measured *ca.* 16 mm., less tentacles. No giant anchors could be seen with a lens on either, nor were there any present in 3 rings of epidermis taken from various parts of the body. The anchors and plates seem to be very typical of the usual shallow water type. A ring of skin of 15 mm. in length by *ca.* 3 mm. in depth, taken from the anterior portion of body, shows *ca.* 95 anchors pointing their flukes in one horizontal direction, and *ca.* 62 to the other, while a very few directed their flukes up or down vertically. Part of the preparation was too opaque to enable all the anchors to be noted. Usually those placed side by side on the strip of skin all point in the same direction, with their flukes opposed to those of the next row; but sometimes 2 or 3 rows will point in one direction against 1 row opposing them. All have nearly straight flukes, with no armature. Those at the posterior end of body are not nearly so crowded. The plates are broad, shield-shaped, with *ca.* 18–32 holes. The perforations in the handle are very variable; sometimes 1 or 2 elongate perforations are present, and at other times a large hole is surrounded, more or less regularly, with smaller holes.

Distribution.—"Probably confined to the coasts of western and southern Europe, and perhaps northern Africa" (Clark, 1907).

Labidoplax Thomsoni (Herapath), 1865.

Synapta digitata (partim) v. Marenzeller, 1893.
„ *thomsoni*, Ludwig, 1898, and Östergren, 1898.
Carrickfergus, Co. Antrim, type, Herapath, 1865.

Clark (1907, p. 97) says:—"Although vouched for by such observers as Herapath and Ludwig, the status of this species is not beyond question. Marenzeller considered his specimens merely as a form of *digitata*." The notes under *L. digitata* of the *Labidoplax* specimens of our hauls show that none possesses the assemblage of characters which are supposed to mark this form, *e.g.*, the absence of giant anchors, and the presence of a secondary network on the plates, and the absence of sensory buds from the tentacles.

I was unable to trace the type specimen, which is not preserved in the museums of Dublin or Belfast. The form has been observed by Ludwig at Naples, in Brittany by Barrois, and in the Adriatic by v. Marenzeller.

Leptosynapta inhaerens (O. F. Müll.), 1776.

Chiridota pinnata, Grube, 1840.
Synapta henslowana, Gray, 1848.
„ *tenuis*, Ayres, 1861.
„ *girardii*, Pourtales, 1851.
„ *pellucida*, Ayres, 1825.
„ *duvernea*, Held, 1857.
„ *ayresii*, Selenka, 1867.
„ *gracilis*, Selenka, 1867.
„ *albicans*, Selenka, 1867.
„ *bifaria*, Semper, 1868.
Leptosynapta tenuis, Verrill, 1867.
„ *girardii*, Verrill, 1874.
Synapta inhaerens, Östergren, 1888; Clark, 1899 and 1901.
(?) „ *albicans*, Clark, 1901.

There is abundant evidence to show that this species lives in sand or muddy gravel, chiefly at L. W. M., at many points all round our coast (Nichols, 1903). We have collected or dredged it ourselves at 24 stations in the north, south, and west of Ireland. Kemp (1905, p. 184) notes that it has rarely been found in more than 30 fms., and on only one occasion (60 fms., off coast of Cork) has this depth been exceeded in our hauls. There are also three records, from as many expeditions, which have taken it in or near our area at depths of 45–96 fms. With regard to the near relatives of *L. inhaerens*, e.g. *L. Galliennii*, Herapath, *L. bergensis*, Östergren, and *L. macrankyra*, Ludwig, Clark (1907, pp. 91 and 92) considers that the Norwegian *L. bergensis* is a synonym of *L. Galliennii*, and adds: "Whether there is an unbroken series between the true *inhaerens* and the Mediterranean *macrankyra* is still uncertain, but for the present we may conveniently recognize the three species . . . . . It is entirely conceivable that under specially favourable conditions in some individuals of *inhaerens*, the anchors and plates might increase in size to that which we find in *galliennii*, and even in *macrankyra*, and in that case the increased number of perforations in the plate would be a natural accompaniment." In his key to the species of *Leptosynapta* (*op. cit.*, p. 87) he says of *inhaerens*, "anchors usually under 250μ, never over 300μ, plates with smooth margins, and not more than 7 or 8 dentate holes"; of *Galliennii*, "anchors not often over 500μ, plates with 7–30 holes"; and of *macrankyra*, "anchors 500–800μ, plates usually with 25 to 40 holes."

The material from our hauls which I have been able to examine includes

specimens from counties Galway and Mayo, collected from L.W.M. to a depth of 11 fms. The anchors varied in size from 176μ, with plate of 154μ, to 297μ, with plate of 210μ. Two anchors, measuring from 308 to 330μ, were also observed; but *ca.* 70 per cent. of the anchors would seem to be under 254μ. The width across flukes is very variable. In 2 anchors, measuring 176μ in length, the width of the flukes varied from 93$\frac{1}{3}$ to 110μ. An anchor of 165μ had flukes of 99μ in width, while those of an anchor of 176μ only measured 93$\frac{1}{2}\mu$ in width. Specimens from Blacksod Bay, collected in the months of March and November, showed many plates with only 7 holes, and others, measuring from 165 to 201μ, possessed as many as 19 holes. The extra holes were small ones at the fixed end of plate, such as figured by Bell (1892 A, Pl. 1, fig. 1), where plates are shown with 7–10 small holes in addition to the 7 large ones.

As regards the development of the gonad, a specimen measuring 25 mm. in length, less tentacles, showed 2 bunches of simple (sometimes forked) gonadial tubes of 2–14 mm. in length. There were 5 tubes in one bunch, and 3 in the other.

Distribution.—Great Britain; Norway to Italy; Bermuda; Main to S. Carolina; Pacific coast, various stations from Washington to California (Clark, 1907).

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PARTICULARS OF STATIONS.

[List of abbreviations:—c. = coarse; f. = fine; g. = gravel; m. = mud; oz. = ooze; s. = sand; sal. = salinity; sh. = shells; st. = stones; temp. = temperature.]

S. 225—22, vi, 1904, outside Lambay Deep, 37–46 fms., f.s., m.

S.R. 151—27, viii, 1904, 54° 17′ N., 11° 33′ W., 388 fms., st., r., bottom temp., 9·15°C.

A. 94—24, i, 1905, off Inisheer, Aran Is., 8 fms.

S.R. 163—2, xi, 1904, 51° 49′ N., 10° 26′ W., 37 fms., g., bottom temp., 12·8°C.

S.R. 222—12, v, 1905, 53° 1′ N., 14° 34′ W., 293 fms., f.s., temp. at 100 fms., 9·9°C.

W. 36—2, ix, 1905, Galway Bay, off north of Inisheer, Aran Is., 16–22 fms., s., sh., bottom temp., 14·7°C.

S.R. 277—15, xi, 1905, 54° 17′ 30″ N., 11° 34′ W., 550 fms., g., sh.

S. 369—22, ii, 1906, 2·9 mi. S.E. by E. of Maiden Tower, Drogheda, 10 fms., s., sh., bottom temp., 5·55°C.

S.R. 327—8, v. 1906, 51° 46′ N., 12° 14′ 30″ W., 550 fms., oz., temp. at 530 fms., 8·95°C., sal. at 500 fms., 35·16 $/_{oo}$.

S.R. 331—9, v, 1906, 51° 12′ N., 11° 55′ W., 610–680 fms., oz.

S.R. 336—12, v, 1906, 51° 19′ N., 12° 20′ W., 673–720 fms., temp. at 700 fms., 6·84°C., sal., 34·99°$/_{oo}$.

S.R. 359—7-8, viii, 1906, 51° 59′ N., 12° 9′ W., 492 fms., oz., temp. at 480 fms., 9·04°C., sal., 35·37°$/_{oo}$.

S. 553—16, viii, 1907, 10 mi. E. of Baily Lt., Howth, 41–52 fms., s., sh.

S.R. 477—28, viii, 1907, 51° 15′ N., 11° 47′ W., 707–710 fms., oz., temp. at 700 fms., 7·19°C.

S.R. 480—28, viii. 1907, 51° 23′ N., 11° 38′ W., 468 fms., st.

S.R. 493—8, ix, 1907, 51° 58′ N., 12° 25′ W., 533–570 fms., oz., temp. at 500 fms., 8·53°C., sal., 35·44°$/_{oo}$.

S.R. 494—8, ix, 1907, 51° 59′ N., 12° 32′ W., 550–570 fms.

S.R. 497—10, ix, 1907, 51° 2′ N., 11° 36′ W., 775–795 fms., oz.

S.R. 500—11, ix, 1907, 50° 52′ N., 11° 26′ W., 625–666 fms., temp. at 600 fms., 8·22°C., sal., 35·41°$/_{oo}$.

S.R. 593—6, viii, 1908, 50° 31′ N., 11° 31′ W., 670–770 fms., oz., temp. at 650 fms., 7·75°C., sal., 35·53°$/_{oo}$.

S.R. 752—16, v, 1909, 51° 48′ N., 12° 11′ 30″ W., 523–593 fms., oz., temp. at 500 fms., 8·9°C., sal., 35·43°$/_{oo}$.

S.R. 851—9, xi, 1909, 50° 48′ N., 11° 41′ W., 900 fms.

S.R. 944—17, v, 1910, 51° 22′ N., 12° 41′ W., 982 fms., oz.

W. 141—13, viii, 1910, off Reenacry Hd., Co. Kerry, 37 fms., g.

S.R. 1176—22, v, 1911, 51° 26′ 30″ N., 11° 2′ W., 100 fms., s.

S.R. 1179—22, v, 1911, 61 mi. W., ½ N. of Blackball Hd., 51° 20′ N. 11° 35′ 30″ W., 456 fms., m., st.

W. 210—21, viii, 1911, 1·7 mi. E.N.E. of Clare Is. Lt., 21 fms., g., bottom temp., 14·46°C.

W. 216—21, viii, 1911, Clew Bay, 3·8 mi. N.E., ½ N. of Carrowmore, 18 fms., r. s., bottom temp., 14·94°C.

S.R. 1391—14, v, 1912, 51° 33′ N., 11° 23′ 30″ W., 149 fms., s., bottom temp., 10·35°C., sal., 35·46°/$_{oo}$.

W. 262—23, viii, 1912, Valentia Harbour, Inside Perch, 7–8 fms., c. s., sh.

S.R. 1456—24, viii, 1912, 51° 35′ N., 11° 43′ W., 405 fms, g., oz.

S.R. 1690—19, viii, 1913, 51° 33′ N., 11° 51′ W., 584 fms.

S.R. 1844—21, v, 1914, 51° 1′ N., 11° 34′ W., 417–565 fms., m., s.

S.R. 1846—22, v, 1914, 51° 26′ N., 11° 45′ 30″ W., 550 fms., s., m., st.

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PHOTOSYNTHESIS AND THE ELECTRONIC THEORY.

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Smithsonian Institution
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MAR 5 1920

V.

PHOTOSYNTHESIS AND THE ELECTRONIC THEORY.

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Introduction.

The most fundamental question in photosynthesis is: "How are the raw materials carbon dioxide and oxygen rendered reactive by chlorophyll when exposed to light?" The answer must be in some way connected with the behaviour of the negative electrons, which, according to modern views, are important constituents of all atoms, and are apparently entirely responsible for the absorption of radiant energy from the aether. The energy absorbed is generally converted into molecular energy, i.e., heat, or otherwise disposed of by the electron, without reaching such a value as to cause the expulsion of the latter from the atom. If, however, the frequency of the incident radiation exceeds a certain limit, depending on the nature of the substance, electrons are actually hurled out of the atoms with very high velocities, the velocity of emission increasing with increase of frequency. This phenomenon, known as the photo-electric effect, is shown most intensely by metals, and in a lesser degree by most other substances. In the case of the alkali metals the limiting frequency is such that the effect can be caused by visible light. With less electro-positive metals and most other substances a higher frequency is necessary, so that ultra-violet light is required. It is obvious that, in order to cause the photo-electric effect, the radiation must be at least partially absorbed.

Following this train of thought, it would appear rational to attribute the conversion of light energy into chemical energy in photosynthesis to the intervention of electrons displaced by the light. The analogy of the

formation of the latent image in the photographic plate suggests itself. Dewar, and subsequently Joly (5), showed that the latent image is produced at extremely low temperatures approaching the absolute zero. This fact, as Joly pointed out, shows that the latent image cannot be produced by the formation of new substances by chemical combination and decomposition, since no such chemical reactions can take place at such low temperatures. Since photo-electricity can be observed at the lowest temperatures, Joly suggested that the latent image is formed by the displacement of electrons, and the ionization so produced revealed when the latent image is converted into the photographic image by development.

On this theory the action of photographic sensitizers is explained somewhat as follows. These bodies, when diffused through, or in contact with, the photographic film, absorb certain wave-lengths, and thus suffer some of their electrons to be displaced. Hence they become ionized, or cause ionization in the surrounding film. This action may be caused by light of a frequency which does not directly affect the silver bromide in the film, so that the presence of the sensitizer renders the plate sensitive to light of a colour that otherwise would not affect it.

According to this view, the photographic film may be used to record the photo-electric properties of the substances admixed with it. In 1874 Becquerel (3) exposed collodium films containing iodide or bromide of silver with chlorophyll (leaf-extract) admixed to the spectrum. With moderate exposures a marked reduction of silver was found in the film after development, in the region of the spectrum extending from E ($\lambda = 527\mu\mu$) into the ultra-violet. Longer exposures and intensification revealed photographic action in a group of bands in the green and a strong band in the red between C and B ($\lambda = 656\mu\mu$ to $\lambda = 687\mu\mu$.) This description coincides closely with the absorption spectrum of leaf-extract according to the recent researches of Willstätter and Stoll (9), and may be looked on as strongly suggesting the photo-electric character of chlorophyll, and as a record of the wave-lengths which are effective in displacing its electrons.

Several researches have been made to ascertain the wave-lengths of light which are utilized in photosynthesis. All investigators are agreed that the wave-lengths between B and C are very effective. Engelmann (4) described a second crest on the curve in the neighbourhood of F ($\lambda = 486\mu\mu$), and much discussion was raised as to the relative effectiveness of wave-lengths of $500\mu\mu$ and less. The work of Kniep and Minder (6), who worked with screens transmitting equal amounts of energy, showed that equal amounts of light energy of wave-lengths of $620\mu\mu$ and more (transmitted through a red screen), or of wave-lengths of $524\mu\mu$ and less (transmitted through a blue screen),

are approximately equal in photosynthetic effectiveness, while the small part of this latter range between 524$\mu\mu$ and 512$\mu\mu$ (transmitted by a green screen) was apparently ineffective. Hence the presence of a second crest on the curve of photosynthesis produced by wave-lengths of less than 500$\mu\mu$, corresponding to the observed sensitizing action to violet light, is definitely established; and we may conclude that the wave-lengths which are effective in displacing the electrons of chlorophyll, as indicated by its sensitizing action on the photographic plate, are the same as those which are effective in photosynthesis. The view that light energy becomes available for photosynthesis through the intermediary of the electrons, arrived at from *à priori* reasoning, is in this way in accordance with experimental results.

The presence of the electropositive element magnesium in the chlorophyll molecule is significant in this connexion.

Granting, then, that the first action of the light is to disturb some of the electrons in the chlorophyll molecule, the question arises as to whether the electrons receive sufficient energy to cause their expulsion from the molecule altogether, or whether the only result is a displacement of the electron within the molecular system itself. In the first case we might suppose chlorophyll to be capable of causing some chemical change in adjacent molecules, without itself taking part in the reaction. In the second, we must consider that its own chemical character is altered by the light, so that it takes a direct part in the resulting reactions. On the first hypothesis we would expect chlorophyll to differ from almost all other substances (except the alkali metals) in showing the photo-electric effect under the action of visible light. Even the light which passes through a red screen should produce an appreciable effect.

PRELIMINARY EXPERIMENTS.

In order to test this point, some preliminary rough experiments were made. Two methods were adopted. In the first, an attempt was made to observe a photo-electric discharge by means of a gold-leaf electroscope, to which was connected an insulated brass plate about 15 cms. square, which could be coated with chlorophyll. Close to this plate and parallel to it was supported a piece of copper wire gauze, which was earthed. An arc lamp was arranged so that a beam of light from it could be so directed as to pass through the gauze and strike the plate. The lamp was at a sufficient distance to prevent the ions generated in the arc from reaching the plate and gauze. When the brass plate was charged positively and the light turned on, no motion of the gold leaf, as observed through a small telescope, was apparent. On the contrary, when the plate and electroscope were negatively charged, the gold

leaf steadily collapsed under the influence of the light. This motion is due to the negative charge being carried off by the expulsion of the electrons from the brass plate by the light, and its rate depends on the photo-electric activity of the brass plate. The plate was now coated with a skin rich in chlorophyll, deposited there by evaporating on it an acetone extract of pulverized nettle leaves. It was then found, on replacing the plate in its former position, that there was no evidence of any photo-electric discharge, no motion of the leaf being observed whether the plate was charged positively or negatively, so that even when acted on by a source rich in ultra-violet light, as the arc is, the chlorophyll gave no evidence of the expulsion of electrons when tested in this manner. The same was, of course, true when the ultra-violet light was cut off by a picric acid screen.

In the second method employed for these preliminary experiments, a change in conductivity was looked for in a medium containing chlorophyll when exposed to light. It seemed possible that, if electrons are expelled by light, their action as current-carriers might be revealed in an alteration of resistance.

In the first instance the sap crushed from leaves was used for this experiment. The sap was introduced into a very narrow, deep, electrolytic cell with glass walls. Into this cell dipped two long platinum electrodes coated with platinum black, connected to a Kohlrausch conductivity apparatus. Measurements of the conductivity when the cell was obscured, and illuminated, indicated no difference of resistance. But the conductivity of the sap is so high compared with the current due to possible photo-electrons that a positive result could scarcely be hoped for in this case, unless the chlorophyll dispersed through the medium possessed a very high photo-electric activity.

A modification of the experiment, using a suspension of colloidal chlorophyll, obtained by diluting an acetone leaf-extract with water, in place of the sap, proved equally negative.

Even when the sap was replaced by a medium having an extremely high resistance a negative result was obtained. Thus no change with illumination could be detected in the current flowing through a small block of paraffin wax in which chlorophyll was dissolved, under a pressure-gradient of nearly 1000 volts per centimetre, the minute leakage current being measured by means of a sensitive electrometer.

We could not, however, expect to detect a very small photo-electric effect by the electroscope method described above. The ordinary gold-leaf electroscope is not very sensitive for small changes of pressure, as several volts are required to cause a motion of the leaf equivalent to one scale division. Its

very small capacity renders it suitable for measuring minute ionization currents when it can be used alone, and not connected to external conductors; but in this case, since a conducting plate is obviously necessary on which to spread the chlorophyll, the advantage of the small capacity of the electroscope itself is, to a great extent, lost. It accordingly seemed to be worth while to repeat the experiments, using an electrometer giving a deflexion of several hundred scale divisions per volt, and magnifying any photo-electric effect by working at reduced air-pressure.

Outline of Electrometer Method.

The usual method was adopted. The substance to be tested was placed on an insulated plate P, enclosed in a testing vessel V, and connected, as shown diagrammatically in fig. 1, to one pair of quadrants of an electrometer E. The other pair of quadrants, the case of the electrometer, and the testing vessel were all connected together and earthed at Z. The grid G was kept at a potential of about + 230 volts by means of a battery of dry cells B. The key K enabled the plate and its pair of quadrants to be earthed at will. The light passed through a window above the grid, and after passing through the spaces in the latter fell on the plate. The difference between the ionization currents with and without the light is a measure of the photo-electric effect.

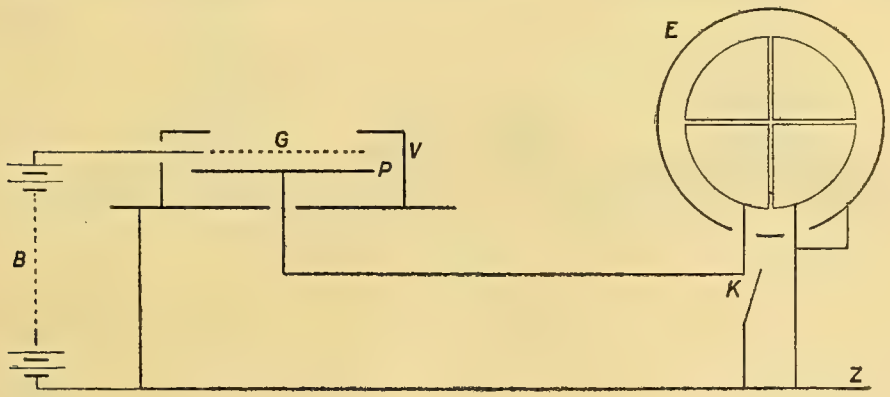

Fig. 1.

Experimental Details.

In initial experiments an appreciable effect was produced when the light was turned on. This was soon found to be spurious, and was traced to the sagging of the grid under the heating effect of the light. A simple calculation shows that a very slight diminution in the distance between the grid and the plate will cause a large effect. For example, in the last experiments

the distance between the grid and the plate was about 4 mm. As the grid is about 5·2 cm. in diameter, the capacity of the condenser so formed would be about $\frac{\pi \times 2{\cdot}6^2}{4\pi \times 0{\cdot}4}$, or about 4 cm. A decrease of the distance between the grid and the plate by 0·1 mm. would increase the capacity by 0·1 cm. As the grid was charged to a potential of about 230 volts, and the plate remained nearly at zero, the increase of negative charge induced on the plate, i.e., the positive charge driven on to the quadrant by the approach of the grid, would be $\frac{230 \times 0{\cdot}1}{300}$, or about 0·075 E. S. U. As will be seen later, one division of the electrometer scale corresponded to $1{\cdot}5 \times 10^{-3}$ E.S.U., so this would cause a deflexion of fifty scale divisions. Obviously then a variation of the distance between the grid and the plate of 0·001 mm. would just cause an appreciable error. It is evident that a wire gauze grid supported at its rim (which was the type used in the experiments referred to) will sag considerably if the central part is even slightly warmer than the rim, as it is certain to be if it is exposed to an intense beam of light. Accordingly, in constructing the testing vessel shown in section in fig. 2, special attention was paid to this point.

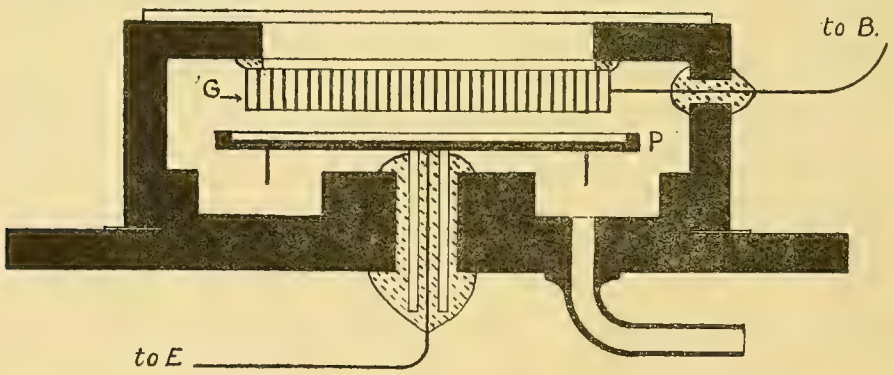

Fig. 2.

The vessel, which is circular in plan, is made in two parts of solid brass sufficiently massive to ensure that its temperature changes only comparatively slowly, especially as its walls are outside the light beam. A thin paper washer is used at the joint, which is sealed with a little warmed tallow. The two parts of the vessel are electrically connected and earthed, thus preventing the possibility of any conduction leakage from the grid to the plate. The vessel is carried on levelling screws not shown in the figure.

The insulated plate has a small rim, as shown, to hold powders, or, is

necessary, liquids. A second rim, placed on the under side, prevents any liquid spilled from reaching the insulation. As the plate is exposed to the light beam, it is important that its support should expand as little as possible, so it is carried on a short quartz tube, which is fixed in a sealing-wax plug passing through the base plate. A thin copper wire down the axis of the tube leads to the electrometer.

The grid, seen in section in the figure, is made of brass strips 6 mm. deep by 0·6 mm. wide, soldered together round the rim. This construction ensures that any expansion of the strips only causes them to curve in a horizontal plane without affecting their distance from the plate. This distance is about 5 mm., so when the plate is covered with leaf-powder or another metal plate the air gap is about 4 mm. Sealing-wax is used to support and insulate the grid and connecting wire, and also to attach the window covering the top of the vessel. In the earlier experiments with this vessel this window was made of glass.

A 500-watt "half-watt" focussing lamp was used as a source, the light being concentrated into a beam of suitable diameter by means of a $4\frac{1}{2}$-inch condenser. A mirror at 45° above the testing vessel reflected the light down on to it. A large beaker full of water standing on the window of the testing vessel acted as a screen to reduce the infra-red radiation; but its presence apparently had little, if any, effect, showing that with this vessel the error due to heating was very small. The beam was so concentrated that almost all of it passed through the window, which is about 5 cms. in diameter.

A battery of sixty pocket-lamp (three-cell) refill dry batteries was used as a source of pressure, the grid being thus kept at about 230 volts. An electrostatic voltmeter (not shown in fig. 1) was connected to the grid to measure its potential and ensure that it remained sensibly constant during a test, as any variation in it would cause a large motion of the electrometer.

The key K (fig. 1) consisted of a mercury cup in a block of paraffin wax fixed on the slate bench on which the apparatus was set up. Into this dipped the wires from the testing vessel and the electrometer, and also a third wire connected to earth as shown. The latter was fixed in such a way that it could be raised out of the mercury by means of a thread passing over pulleys, thus isolating the quadrant system. The act of breaking contact generally caused a deflection of the electrometer, which varied both in magnitude and direction; but readings were never started until the disturbance so caused had died down, and the electrometer spot of light was steady near its zero position. The key also served for connecting another wire for charging the quadrant to some known pressure (generally 0·5 volt) for calibration.

The electrometer is of the Dolezalek type, with a coarse quartz suspension. The needle was always charged to about + 300 volts by means of a hygroscopic battery before commencing a set of readings, and the sensitivity tested. This varied somewhat from day to day, ranging between about 340 and about 370 scale divisions per volt, but only fell a few per cent. during a set of readings, as the insulation of the needle was very good. The wires connecting the testing vessel and the electrometer to the key were each about 25 or 30 cms. long. They were everywhere within a few centimetres of the slate bench, which, being a conductor, acted to a certain extent as a protection against electrostatic induction effects; but, as it was not necessary to approach the apparatus during a test, no other electrostatic screen was used. A wooden screen was interposed between the testing vessel and the electrometer to protect the latter from possible heating effects. The connecting wires passed round the end of this screen.

A double-barrel Geryk pump was used to exhaust the testing vessel, the air-pressure being measured on a mercury gauge by means of a reading microscope. By reducing the pressure the photo-electric current can be magnified by collision and the sensitiveness greatly increased.

It has been shown (see Allen, "Photo-Electricity," p. 64) that the pressure p which gives the maximum magnification is given by the relation $p = \frac{E}{dNV}$, where E is the voltage applied to the grid, d the distance from grid to plate, N the number of collisions made by one electron per centimetre at a pressure of 1 mm. of mercury, and V the potential difference through which an electron must fall in order to produce fresh ions at impact. In this case E was about 230 volts, and d about 0·4 cm. For air N = 14·6, and V = 25 volts [Townsend (8)], which gives p = 1·6 mm. of mercury. Most of the experiments were carried out at a pressure of 2 mm. of mercury, which is sufficiently close to the calculated value to give nearly the maximum magnification. The maximum current is equal to $\iota e^{\frac{E}{Ve}}$, where e is the base of the natural system of logarithms, and ι is the current due to the photo-electrons emitted. Putting in the above figures, we find that the maximum current is 29·3ι, so we may assume that working at 2 mm. the magnification is nearly thirty-fold. This is borne out by a test on a zinc plate, in which the current at 2 mm. pressure was about forty-five times that at atmospheric pressure. This latter would be considerably smaller than the full value corresponding to the photo-electrons emitted, as a certain number of them would diffuse back to the plate in spite of the applied electric field, so the agreement is quite satisfactory.

To test the capacity of the plate-quadrant system, the deflexion produced

by suddenly applying a known pressure of a few volts to the grid was found. The grid was earthed, and the plate system isolated, and a reading of the spot of light was taken. The grid was then raised to a known small pressure. The induced charge caused a motion of the electrometer, which was again read as soon as it had become steady. The grid was then earthed, thus causing the spot of light to return nearly to its original position. The difference between the second reading and the mean of the first and third measures the rise in potential of the plate and quadrants for a known rise of the grid.

The entire system may be regarded as two condensers of capacities K_1 and K_2 in series. K_1 is the capacity of the condenser formed by the grid and the plate, and K_2 that of all the rest of the system, including the lateral capacity of the plate and wires, and the effective capacity of the electrometer quadrants. If V is the applied voltage, and E_1 the pressure indicated by the electrometer, evidently $(V-E_1)\,K_1 = EK_2$, since the charges on two condensers in series must be equal. Hence $\frac{K_1 + K_2}{K_1} = \frac{V}{E_1}$. Since we can calculate K_1 approximately, we can find $K_1 + K_2$, which is the capacity of the system when the grid is at a fixed potential, as in the actual test. As, however, K_1 can only be found rather roughly, this method is not accurate, so the readings were repeated with an air-condenser of known capacity K_3 connected in parallel with the electrometer, whose voltage was now found to rise to E_2. Hence

$$\frac{K_1 + K_2 + K_3}{K_1} = \frac{V}{E_2}; \quad \text{so} \quad \frac{K_1 + K_2 + K_3}{K_1 + K_2} = \frac{E_1}{E_2}, \quad \text{or} \quad K_1 + K_2 \quad \frac{E_2K_3}{E_1 - E_2}.$$

By this method the effective capacity of the system was found to be about 167 cms. On this occasion the sensitivity of the electrometer was, for small motions, about 372 scale divisions per volt, so that one scale division corresponded to $\frac{167}{300 \times 372}$, or $1{\cdot}50 \times 10^{-3}$ E. S. U. of charge. Hence one scale division per minute represents a current of $2{\cdot}5 \times 10^{-5}$ E.S.U., or about 8×10^{-15} ampere. This will not be very much affected by small variations in the voltage of the electrometer needle, as the large effective capacity of the electrometer is chiefly due to inductive effects caused by the motion of the charged needle, and a small change in the charge on the latter will affect the sensitivity (which increased with the potential of the needle) and the capacity to about the same extent.

In making a test the plate system was isolated and the lamp turned on, the beam of light being cut off by a cardboard shutter. As soon as the electrometer had become steady near its zero position, it was read and a stop-watch

started. At the end of a certain period, generally three minutes, another reading was taken, and simultaneously the shutter was raised by means of a thread, thus allowing the beam of light to fall on the substance on the testing plate. After another three minutes a third reading was taken and the shutter replaced, and so on, thus finding the motion of the spot of light during alternate periods, in which the substance under test was alternately illuminated and in darkness. The motion during the "dark" intervals is chiefly due to the natural ionization of the air in the testing vessel. During the "light" intervals this is increased by the photo-electric current, if any. The mean difference between the movements during the "light" and the "dark" intervals is a measure of the photo-electric current.

The following is a typical set of readings, obtained when the plate was covered as uniformly as possible with a layer of freshly prepared leaf-powder about 1 mm. thick. The air-pressure in the testing vessel was kept very close to 2 mm. of mercury throughout. The sensitivity of the electrometer was such that 0·5 volt produced a deflexion of 179 scale divisions, and the pressure of the grid was 231 volts. The interval between readings was three minutes:—

Movement in 3 mins. "Light."	Electrometer Reading. (zero 200.)	Movement in 3 mins. "Dark."
	213	
		3
	216	
3·5		
	219·5	
		2
	221·5	
3		
	224·5	
		2
	226·5	
2·5		
	229	
		1·5
	230·5	
2		
	232·5	
		1
	233·5	
Total, 11 in 12 mins.		Total, 9·5 in 15 mins.
Rate per min. 0·92.		Rate per min. 0·63.

It will be observed that, as the deflexion increases, the rate of motion decreases. This always occurs, and is chiefly due to the leakage of the

electrometer quadrants. This decrease does not appreciably affect the difference caused by the light. In this case the increase caused was about 0·3 scale division per minute, representing a current of 7×10^{-6} E.S.U.

The following table shows the results obtained with different substances :—

Substance on Test Plate.	Current in E. S. U.
Leaf-powder kept in the dark in a stoppered bottle for 9 months,	8×10^{-6}
,, freshly prepared, ...	7 ,,
Zinc plate coated with chlorophyll from acetone solution, .	7 ,,
Same a second test at 1·5 mm. air pressure, . .	4 ,,
Zinc plate coated with colloidal chlorophyll from acetone and water solution, ...	9 ,,
Same with red screen interposed in path of light beam, .	1 ,,
Zinc plate freshly cleaned with carborundum cloth (at 2 mm.),	600 ,,
Same at atmospheric pressure, ...	11 ,,
Same with pressure again reduced to 2 mm., . . .	370 ,,

In these tests the air-pressure, unless otherwise stated, was 2 mm. The last three figures show how very much more active the zinc plate was than the chlorophyll, and indicate the presence of a certain amount of ultra-violet light, in spite of all the glass in the path of the beam. They also show the very great increase in the current caused by reducing the pressure, and also the photo-electric fatigue of the zinc.

The red screen used in one test was a Wratten gelatine colour filter, No. 29. This test, which was not a very satisfactory one, as the electrometer movements were slightly irregular, shows that the light which passes through the screen produces little, if any, effect.

TESTS WITH A SOURCE RICH IN ULTRA-VIOLET LIGHT.

As M'Clelland and FitzGerald (7) obtained a considerable photo-electric effect with leaf-extracts, using the light from a spark, it seems probable that the small effect shown above is due to the ultra-violet light which passes through the glass. It appeared to be worth while to repeat some of the tests with a source rich in ultra-violet light.

Accordingly the half-watt lamp was replaced by an open carbon arc, and a quartz condenser substituted for the glass one. A quartz window was fitted to the testing vessel, and a speculum metal mirror used instead of the silvered glass one. The water beaker was removed, and heating was reduced by using a much less concentrated beam than before. The rest of the apparatus was unaltered.

It soon became evident that the activity was enormously increased, so that the natural leak of the testing vessel was negligible. In making tests with chlorophyll the plate system was isolated, and a reading taken with the arc burning, but shuttered off. The shutter was then raised for about ten seconds, as timed with a stop-watch, and then replaced. The electrometer spot of light soon became almost stationary again, and the difference between the two readings measured the effect for the time that the light was acting. From this the displacement per minute, and so the current, was found. This varied considerably in different tests, the variations being probably chiefly due to changes in the arc. When a clean zinc plate was used the shortest flash of light that could be given sent the electrometer off the scale. A condenser of capacity $\frac{1}{3}$ microfarad was put in parallel with the electrometer, thus reducing the sensitiveness to about $\frac{1}{1800}$th part of its previous value. An exposure of about half a minute then produced a convenient deflexion. The results obtained are shown below :—

Substance on Test Plate.	Current in E. S. U.
Zinc plate coated with chlorophyll, . . .	12×10^{-3}
Layer of leaf-powder about 1·5 mm. thick, . .	16 ,,
Clean zinc plate, ...	6650 ,,

It will be seen that the chlorophyll is about 2000 times, and the zinc over 10,000 times, as active with this source compared with the previous one. The interposition of the red screen reduced the activity almost, if not quite, to zero. The measurement of very small currents could not be made quite so accurately as before, as the motion of the electrometer needle was not quite so regular. The variations were probably due to draughts of slightly ionized air from the arc reaching the connecting wires.

Discussion of Results.

All the evidence points to the fact that the extremely small effect obtained with the "half-watt" lamp was due to the small amount of ultra-violet light present. The last test shows that the latter produces a pronounced effect. The light which passes through the red screen is apparently inactive. Now, this red light is very effective in causing photosynthesis, so apparently photosynthesis is caused by light whose frequency is too low to effect the expulsion of an electron from the chlorophyll molecule.

This conclusion is greatly strengthened when we consider quantitatively the results obtained. The largest photo-electric current obtained with leaf-powder illuminated by the "half-watt" lamp was about 9×10^{-6} E.S.U. Let us assume that the current was magnified twenty times by collision—an estimate which, in view both of the results obtained with the zinc plate and of the value

deduced theoretically, is almost certainly too low. The current due to the actual photo-electrons emitted must then have been $4{\cdot}5 \times 10^{-7}$. As the electronic charge is $4{\cdot}774 \times 10^{-10}$ E. S. U., this corresponds to the emission of 940 electrons per second from the illuminated surface. The effective area of this was about 12·5 square centimetres, allowance being made for the part shaded by the grid, so the number of electrons per square centimetre per second works out at 75. This, which is probably an over-estimate, corresponds to the emission of 27×10^8 electrons per square metre per hour. It is most unlikely, in view of the small amount of energy available, that one electron could cause the assimilation of more than one atom of carbon. In fact, the energy quantum for red light of frequency 5×10^{14} is about $3{\cdot}3 \times 10^{-12}$ erg, while the energy required to decompose one molecule of carbon dioxide is about $6{\cdot}6 \times 10^{-12}$, i.e. equal to two quanta. This figure refers to gaseous carbon dioxide, and may need modification in the case of dissolved carbon dioxide. But if we assume that each electron causes the assimilation of one atom, we are not likely to be under-estimating the quantity of carbon assimilated. Taking the mass of the hydrogen atom as $1{\cdot}65 \times 10^{-24}$, this comes out as $5{\cdot}3 \times 10^{-14}$ gram per square metre per hour. This is an utterly negligible figure in comparison with the quantity actually assimilated in strong sunlight, which is of the order of half a gram per square metre of leaf-surface per hour.

The leaf-powder used was not treated chemically in any way. The leaves were merely dried at a moderate temperature in an air-oven, and powdered. Willstätter and Stoll (9) have shown that the chlorophyll is not altered chemically by this treatment.

As the energy of photo-electrons due to visible light would be so small, it seems unlikely that their range in the leaf-powder would much exceed the distance between two adjacent atoms, so we would only expect those chlorophyll molecules which are actually on the surface to contribute to the photo-electric current. As, however, the diameter of an atom is of the order of 10^{-8} centimetre, it seems incredible that only about one in 10^{13} of the chlorophyll molecules in a layer of powder one millimetre thick is on the surface. Even then we would have to assume that the activity of the living leaf is equivalent to that caused by all the chlorophyll in such a layer.

CONCLUSION.

The experiments recorded above show that those wave-lengths of light which are effective in photosynthesis are unable, to any appreciable extent, to expel electrons from the leaf-pigment complex, and hence cannot in this way produce ionization, or bring about reactions external to the pigment.

The action apparently occurs within the molecule of the chlorophyll itself. Possibly electrons are transferred from one atom to another, thus altering the linkage, and hence the chemical nature of the molecule, or its atomic groups.

It is also conceivable that electrons might be transferred from molecules of chlorophyll to adjacent molecules, whose presence is necessary to facilitate the escape. Such an action could hardly be classed as photo-electric, using the term in its ordinary sense, and would not be detected by the method employed.

If it is shown that chlorophyll acts like other sensitizers, and affects the sensitiveness of the photographic plate even when it is removed before development [Abney (l)], such a transference of electrons from the chlorophyll to one of the other constituents of the photographic film seems a necessary assumption.

The constant association of the four pigments

Chlorophyll *a* ($C_{55}H_{72}O_5N_4Mg$), Chlorophyll *b* ($C_{55}H_{70}O_6N_4Mg$),
Xanthophyll ($C_{40}H_{56}O_2$), and Carotin ($C_{40}H_{56}$)

in sensibly constant proportions, in the chloroplasts of green plants, as shown by Willstätter and Stoll (9), and the chemical relationship of these substances, elucidated by the same investigators, pointedly suggest a transference of electrons between the components of the pigment complex in the chloroplast securing the ultimate reduction of the carbon dioxide and the liberation of oxygen. This transference must be effected directly or indirectly by the light. Any evidence as to the nature of this process and the interdependence of these substances is so desirable that it is hoped shortly to repeat our observations on pure samples of the individual pigments, instead of using the crude leaf-extract or leaf-powder. It seems, however, rather unlikely that a positive result will be obtained with the separate pigments, since the result with the complex was so decisively negative.

For the present, then, it appears we must assume that the atomic groups of the leaf-pigment enter into the reaction of photosynthesis, and participate in the combinations and decompositions which ultimately lead to the formation of carbohydrates and the evolution of oxygen. The experimental evidence seems to debar us from regarding the pigments in the chloroplasts as mechanical contrivances for effecting the ionization of molecules external to themselves. Thus the chemical theories of photosynthesis, such as Hoppe Seyler's and Willstätter's, which assume that the chlorophyll itself enters into the reactions, are to be preferred to those suggestions, like Siegfried's, which suppose that the reaction is accomplished externally to the chlorophyll by means of the energy absorbed and transformed by the latter.

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VI.

NOTE ON THE DECAY OF MAGNETISM IN BAR MAGNETS.

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Section 1.

At a meeting of this Society on December 21st, 1909, the writer read a paper on "Permanent Steel Magnets." Section 1 of that paper dealt with the dimension-ratios of the magnets which were made of the same kind of steel, and Section 2 with the moments of magnets made of steels of various chemical composition. These magnets in Section 2 only are dealt with in the present communication; and at that time (about ten years ago) they were tested for magnetic moment per gramme at intervals for six months, and the percentage loss in magnetic moment for a period of six months measured. The magnets were then put away from all disturbing influences, and have remained in a vertical position for about ten years, and have now been re-tested for magnetic moment, with the results given in this note.

The details of the tests and the heat treatment of the magnets are given on pp. 316–320 of the paper referred to, and the results now obtained are given and compared with the previous results, that is, the percentage loss in the magnetic moment per gramme for each magnet for a period of about ten years.

The magnets were 8 cms. or 10 cms. long and 0·3 cm. diameter, giving dimension-ratios of 27 and 33, as shown in Table I.

In Table I the numbers 1 and 6 are left out, as these referred to magnets made of practically pure iron, and were used in the previous paper merely as standards of reference.

[1] Scient. Proc. Roy. Dublin Soc., February, 1910, vol. xii, pp. 312–320.

SCIENTIFIC PROCEEDINGS.

VOLUME XVI.

1. A Cryoscopic Method for the Estimation of Sucrose. By HENRY H. DIXON, SC.D., F.R.S., and T. G. MASON, M.A., SC.B. (January, 1920.) 6*d.*
2. The Carboniferous Coast-Section at Malahide, Co. Dublin. By LOUIS B. SMYTH, B.A., SC.B. (Plates I., II.) (February, 1920.) 1*s.*
3. The Application of the Food-Unit Method to the Fattening of Cattle. By JAMES WILSON, M.A., B.SC. (Plates III., IV.) (February, 1920.) 1*s.*
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NOTE ON THE DECAY OF MAGNETISM IN BAR MAGNETS.

Smithsonian Institution
MAR 5 1921
National Museum

BY

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[*Authors alone are responsible for all opinions expressed in their Communications.*]

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MAR 5 19

TABLE I.

No.	Chemical Composition.						$\frac{l}{d}$				
	C	Mn	Si	Ni	W	Cr		*A*	*B*	*C*	*D*
2	1·09	0·32	0·06				27	21·4	20·0	21·1	1·4
3	0·75	1·00					,,	31·2	6·8	26·2	16
4	0·50	1·00		1·00			,,	27·5	10·1	26·4	4
5	1·30	3·09				8·92	,,	26·4	14·0	24·9	6
7	0·22	0·18	0·44				33	25·0	11·0	22·2	11·2
8	0·26	0·18	0·33	0·58			,,	27·5	7·4	20·3	26
9	0·28	0·28			3·5		,,	22·4	6·6	21·1	5·8
10	0·76	0·28			15·5		,,	38·5	2·7	32·5	15·5
11	0·40	2·25			3·25		,,	29·6	11·6	27·0	8·8
12	0·25				2·00	0·75	,,	30·0	14·0	26·9	10·3
13	0·43					3·25	,,	34·5	3·6	26·5	23·2
14	1·09					9·50	,,	27·5	10·4	23·6	14·2
15	0·25			2·75		0·75	,,	15·0	15·2	14·3	4·7
16	0·31			2·50		1·75	,,	30·2	9·6	25·1	16·8

A = Magnetic moment per gramme in December, 1909, or six months after being magnetized.
B = Percentage loss in magnetic moment six months after being magnetized.
C = Magnetic moment per gramme in January, 1920.
D = Percentage loss in magnetic moment for a period of about ten years, or from December, 1909, till January, 1920.

It will be seen from the table that No. 2 magnet has lost very little of its magnetism after the first six months, and seems to have settled down to a practically permanent state. The fairly high carbon and manganese makes this a good permanent magnet, though its actual moment is not very high.

Comparing Nos. 3 and 4, which have the same amount of manganese and fairly high carbon, the latter, having also 1 per cent. of nickel, has four times the retentivity of the former, though the percentage loss in the six months after being magnetized is nearly double of that in No. 3. Taking Nos. 2 and 14, which have the same amount of carbon, and the latter a high percentage of chromium, the presence of the chromium has reduced the retentivity ten times, which confirms a result given by the writer in another paper, namely, that more than about 2·5 per cent. of chromium in steel decreases its value as a magnet.[1]

[1] Scient. Proc. Roy. Dub. Soc., April, 1910, vol. xii, pp. 349-353.

Comparing Nos. 5 and 14, which have high carbon and a high percentage of chromium, the former having also over 3 per cent. of manganese, we see that the percentage loss in No. 5 is less than half that in No. 14, due no doubt to the presence of the manganese.

Of the four tungsten steels, Nos. 9 to 12, inclusive, the first seems the best from the point of view of retentivity; and it is known that a steel containing about 7·5 per cent. of tungsten makes the most permanent magnet;[1] and No. 9, though the actual magnetic moment is low, is a fairly permanent magnet. No. 15 is a good magnet, though its moment is low compared with No. 16, which has 1 per cent. more of chromium; the retentivity of the former is over three times that of the latter.

In the paper above referred to (April, 1910), in Table IV, page 318, it was shown that the magnetic moments all increased slightly one month after they had had the final five hours' annealing by steam, so that if we were to calculate the total loss from that time, July, 1909, till now, January, 1920, the magnets, with the exception of No. 8, arrange themselves into three natural groups, as shown in Table II, where Column *E* gives the total percentage loss in ten and a half years.

TABLE II.

No.	*E*
2	26·4
3	25·8
4	27·0
5	24·8
7	25·0
9	17·2
10	21·7
11	21·3
12	27·9
13	32·0
14	28·5
15	23·5
16	28·9

From 2–7, manganese steels, the loss is about 25 per cent.; from 9–11, tungsten steels, the loss is about 20 per cent.; and from 12–16, chrome steels, the mean loss is over 25 per cent.

[1] Scient. Trans. Roy. Dub. Soc., vol. vii, Plate vi, January, 1900.

SECTION 2.

In February, 1910, the writer read a paper before this Society on "Chrome Steel Permanent Magnets," where results were given for seven magnets of dimension-ratio 33, the magnets containing different percentages of chromium.[1] They were then tested for magnetic moment per gramme when in the condition (1) glass-hard, (2) annealed, and also tested for the percentage loss in the moment due to percussion. The details of the tests and the heat-treatment of the magnets are given in the paper referred to. The magnets in the annealed state were put carefully away after the tests, and have remained undisturbed from that date to this, or about ten years, when they have again been tested for the decay of magnetism, with the results here given.

In Table III the results in column *A* are the values of the moments when the magnets were stored away ten years ago, that is, they are the values given in the paper referred to above, *minus* the percentage loss due to percussion in each case.

TABLE III.

No.	Chemical Composition.									
	C	Si	Mn	Cr	W	Cu	*A*	*B*	*C*	*D*
1	0·88	0·19	0·28	1·75			40·4	36·8	8·9	1·9
2	0·86	1·96	0·40	1·96			50·3	43·6	13·3	0·5
3	0·76	1·02	0·29	2·11			50·7	48·2	5·3	2·2
4	0·54	2·20	0·22	3·50			38·1	34·2	10·2	7·9
5	0·85	0·31	0·50	5·79		1·83	36·5	35·0	4·1	7·0
6	1·36	0·75	2·60	9·22			42·7	40·1	6·3	1·3
7	0·48	0·29	0·82	1·74	1·90	1·91	40·0	35·3	11·7	3·2

A = Magnetic moment per gramme in January, 1910.
B = ,, ,, ,, ,, 1920.
C = Percentage loss in the moment for a period of about ten years.
D = Total percentage loss due to percussion from previous paper, p. 351.

It has been stated by Mme. Curie that small quantities of silicon have little or no effect on the magnetic properties of a magnet.[2]

[1] Scient. Proc. Roy. Dub. Soc., April, 1910, vol. xii, pp. 349-353.
[2] Bull. de la Société d'Encouragement, pp. 36-76.

By comparing Nos. 1 and 2 in the table, it looks as if the high silicon in No. 2 had decreased its retentivity; the same appears to apply to No. 4. Taking Nos. 1 and 7, with nearly the same amount of chromium, the smaller carbon and larger manganese in No. 7 seem to counteract each other; also, the equal quantities of tungsten and copper neutralize to make the retentivity of the magnet poor.

The magnets 3, 5, and 6 are good, and confirm an observation made by the writer, and given in the paper referred to above, that the best proportion of chromium for a magnet was about 2·5 per cent.; the results for No. 3 magnet more nearly illustrate the fact. The actual moment per gramme of No. 5 is low, though its retentivity is high, due possibly to the presence of copper neutralizing the chromium, as well as its fairly high carbon. On the whole it is evident, as far as permanence is concerned, that the best magnets would be Nos. 3, 5, and 6.

Column *D* in Table III gives the total percentage loss in the magnetic moment per gramme due to the magnets being allowed to fall, end on, from the height of one metre *four times* on to a block of glass; in every case with the *true north* or *south pointing* pole downwards.

SCIENTIFIC PROCEEDINGS.

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1. A Cryoscopic Method for the Estimation of Sucrose. By HENRY H. DIXON, SC.D., F.R.S., and T. G. MASON, M.A., SC.B. (January, 1920.) 6*d*.
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ON THE INHIBITION OF INVERTASE IN THE SAP OF *GALANTHUS NIVALIS.*

BY

T. G. MASON, M.A., Sc.B.

Smithsonian Institution
MAR 5 1921
National Museum

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VII.

ON THE INHIBITION OF INVERTASE IN THE SAP OF *GALANTHUS NIVALIS.*

By T. G. MASON, M.A., Sc.B.

Read February 24. Published April 12, 1920.

In view of the widespread occurrence of invertase in the leaves of plants (8), it seemed probable that an approximate estimate of the sucrose-content of the sap could be obtained by observing the increase in depression of the freezing-point after storage at a suitable temperature.

As a 1 per cent. solution of sucrose has a depression of 0·054° C., whereas after its hydrolysis to invert sugar it has approximately double this depression, a method is provided of recording the amount of sucrose inverted (7).

The experiments were carried out on the Snowdrop (*Galanthus nivalis*), and, as starch and inulin are absent from its leaves (10), the difficulties which might be introduced by the production from these sources of maltose, dextrose, and levulose need not be considered.

In the earlier experiments made on this matter it was found that other factors, which tended to limit the activity of the enzyme, were present; consequently it was considered that an investigation of their nature might prove of interest.

The freezing-point determinations were made by means of Dixon's thermo-electric method (4 and 5).

The saps for the freezing-point determinations shown in Table I were pressed from tissues rendered permeable by exposure to intense cold. To do this the leaves were rolled and packed in test-tubes, which after sealing were immersed for two hours in a freezing mixture of salt and ice (–16° C.).

The white bases of the leaves were rejected, and the sap, as pressed from the leaves, was collected in test-tubes fitted with an ice-jacket to prevent inversion.

Sap was also pressed from leaves which had not received any treatment.

As soon as the freezing-point determinations were made the saps were stored for approximately twenty-four hours at 29° in a thermostat.

The increases in depression are shown in Table I in the last column [$\Delta_2 - \Delta_1$].

In the absence of other changes affecting the depression, this increase should afford a measure of the sucrose inverted.

TABLE I.

Description of Sample.	Treatment.	Δ_1	Δ_2	$\Delta_2 - \Delta_1$
Leaves collected 9.30 A.M., March 21st. Snow in night and on previous day.	Untreated.	0·576°	0·627°	0·051°
	Frozen.	0·888°	0·943°	0·055°
Leaves collected 9.15 A.M., March 24th. Dull and wet previous day.	Untreated.	0·544°	0·655°	0·111°
	Frozen.	0·834°	0·940°	0·106°

That sap pressed from tissues which have been exposed to intense cold has a much greater depression of the freezing-point than that from untreated material has been already demonstrated by Dixon and Atkins (5), and does not call for further comment. On the other hand, it will be noted that the increase in depression after storage is as great in the sap pressed from untreated leaves as in that from the frozen material.

Assuming the increase in depression is proportional to the sucrose-content of the sap, this might be due to the greater permeability of the protoplasm to sucrose than the other solutes; or else that in the pressing of the untreated leaves the rupture of the cells has set free the contents of the larger vacuoles, where possibly the concentration of sucrose is greater than in the protoplasm.

In Table II the results of a somewhat similar experiment are shown. Sap pressed from leaves, both untreated and frozen, was again employed, but in this case, with a view to determining if the acidity of the sap was responsible (by hydrolysing the sucrose) for any of the rise in depression on storage, a sample of each was immersed with its containing test-tube for one minute in boiling water; a reflux condenser was fitted to each test-tube.

TABLE II.

Description of Sample.	Treatment.	Δ_1	Δ_2	$\Delta_2 - \Delta_1$
Leaves collected 9.30 A.M., March 28th. Previous day bright and showery.	Untreated.	0·552°	0·610°	0·058°
	Do., boiled.	0·553°	0·553°	—
	Frozen.	0·904°	0·924°	0·028°
	Do., boiled.	0·891°	0·888°	—

The acid of the sap has evidently not been responsible for the rise in depression observed in the samples which were not boiled. The increase in depression in the sap pressed from untreated leaves is in this case much greater than that from the frozen.

It is clear from a survey of Tables I and II that, if the increase in depressions of the sap pressed from the frozen material were an index to the sucrose-content, very great fluctuations must have taken place in a comparatively short time.

It is instructive to compare the increases in depression recorded in Tables I and II with those found by Dixon and Atkins (5) (Table III) on storing sap pressed from untreated leaves of *Syringa vulgaris*. The material for these experiments was collected towards the close of October; the saps were pressed from unfrozen leaves, and were filtered and stored at room-temperature.

TABLE III.

No. of Experiment.	Description of Sample.	Δ_1	Δ_2	$\Delta_2 - \Delta_1$
66 and 67	Gathered 2.30 P.M., after sunny morning.	1·215°	1·220°	0·005°
71 and 73	—	1·424°	1·540°	0·116°

Here similar great differences in the change in depression on storage are noticeable.

As it was considered possible that the fluctuations observed in the increase in depression of the freezing-points on storage might not be

unconnected with the presence of micro-organisms on the surface of the material, some leaves were immersed for six days in a little freshly boiled water. The water was then decanted off, and to 220 c.c. were added 7·7 gms. of sucrose. The solution was divided into two parts, one of which was boiled. Both were saturated with toluene. After nine days' incubation at 29° C., there was no evidence of inversion in either sample; thus the enzymes set free from micro-organisms do not appear to have been responsible for any of the rise in depression recorded in Tables I and II.

In the next experiment the leaves of a clump growing in the open were divided into three parts. The leaves were gathered at 10 a.m. on April 30th. The first sample was pressed immediately without any treatment, the second was exposed to toluene vapour for five hours in a sealed chamber, while the third, enclosed in a test tube, was immersed in a salt-ice freezing mixture (−16°) for two hours. About 60 c.c. of sap were collected from each sample, and filtered and stored overnight at 0°.

The depressions of freezing-point and the electrical conductivities are shown in Table IV. The conductivity observations were made at 0°, and are liable to a correction allowing for the viscosity of the saps. As the saps were saturated with toluene, 0·02° (the depression of the freezing-point of water saturated with toluene) has been subtracted from the observed depressions. Toluene was not added to the saps on which the conductivity measurements were made.

TABLE IV.

Treatment.	Δ	c. × 10^5
Frozen, ...	0·818°	630
Toluene, ...	0·710°	547
Untreated, ...	0·528°	336

That exposure to toluene vapour has not rendered the protoplasm completely permeable is indicated by the greater depression of the sap pressed from the frozen leaves; the difference, however, may be due to a partial destructon of sugar owing to the stimulation of respiration by the anæsthetic.

On immersing the three samples of sap for one minute with their

containing test-tubes in boiling water, the variation in the amount of protein precipitated was very marked. The amount in the sap pressed from the untreated leaves was almost double that of the frozen, while that from the toluene material was very slight. On storage at room-temperature differences in the amount of precipitated colloids of the same order were observed in the untreated and frozen samples, though none could be detected in that pressed from the toluened leaves.

With ferric chloride a dark green colouration was produced in all samples, but, as gelatine was not precipitated, it is improbable that a true tannin was present.

The changes in the depression of the freezing-point during a storage of seventy-two hours at 29° are shown in Table V.

The term "sap + sucrose" in the table refers to samples in which 25 c.c. of each sap were added to two grams of sucrose.

Both the saps and the sap + sucrose solutions were stored in small flasks, previously sterilized, and fitted with rubber corks. A little toluene was added before each observation in order to ensure that the samples were completely saturated.

To make an observation 5 c.c. were withdrawn from each flask, and stored at 0° till all the observations were complete. The samples used for the determinations of the freezing-points were then returned to their respective flasks.

TABLE V.

Treatment.	Description of Sample.	No. of Hours.			
		Δ_0	Δ_{24}	Δ_{48}	Δ_{72}
Frozen,	Sap,	0·838°	0·872°	0·866°	0·858°
	Sap + Sucrose,	1·318°	1·358°	1·352°	1·363°
Toluene,	Sap,	0·730°	0·735°	0·739°	0·741°
	Sap + Sucrose,	1·209°	1·207°	1·219°	1·216°
Untreated,	Sap,	0·548°	0·576°	0·606°	0·582°
	Sap + Sucrose,	1·015°	1·053°	1·108°	1·117°

Figures 1, 2, and 3 show these changes in the depression of the freezing-point graphically represented. The depressions on the left and right of the figs are those of the sap + sucrose solutions and saps respectively.

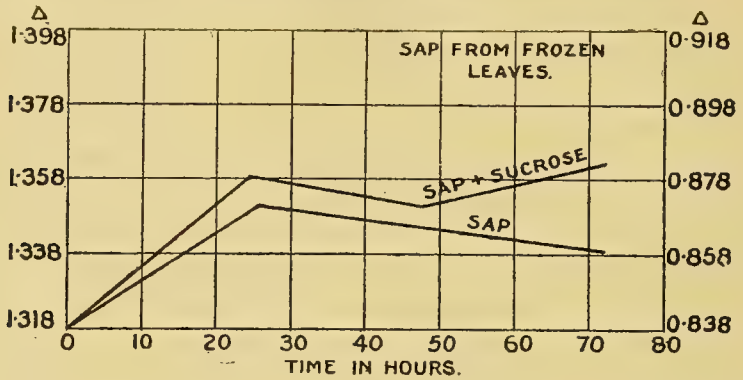

Fig. 1.

The increase in the depression of the freezing-point of both frozen and untreated samples is, doubtless, due to the inversion of sucrose; the interpretation of the subsequent changes in the depression is not clear. The presence of factors inhibiting the hydrolysis of sucrose is, however, indicated. In the toluened samples this is very marked, but, as there is very little indication of any hydrolysis, it may be that exposure to toluene vapour has

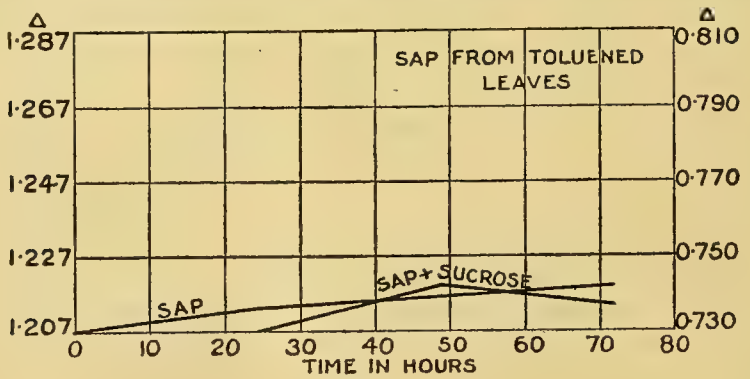

Fig. 2.

destroyed the enzyme. That this is unlikely is indicated by the fact that toluene has no toxic effect on the invertase of yeast. It may not be without significance that the amount of sucrose inverted in the three samples is roughly proportional to the colloids precipitated on storage. The clumping of the colloids of the sap after its extraction from the leaf is very striking, and has been observed in the extracted sap of a number of plants.

It was considered possible that the addition of a little saponin to the

toluened sap + sucrose solution might, by lowering the surface-tension, free the enzyme if present from any adsorbent colloid.

No increase in hydrolysis could, however, be detected in the samples treated with saponin.

This need not negative the adsorption view of the inhibition, as not only is there evidence that a saponin is normally present in the sap, but the adsorption might well be specific.

The absence of a precipitation of colloids on storage from the toluened samples suggests that the precipitation may have taken place in the cell-vacuoles during the exposure of the leaves to toluene vapour, and that possibly the enzyme was removed with the colloids, and therefore was not extracted with the sap.

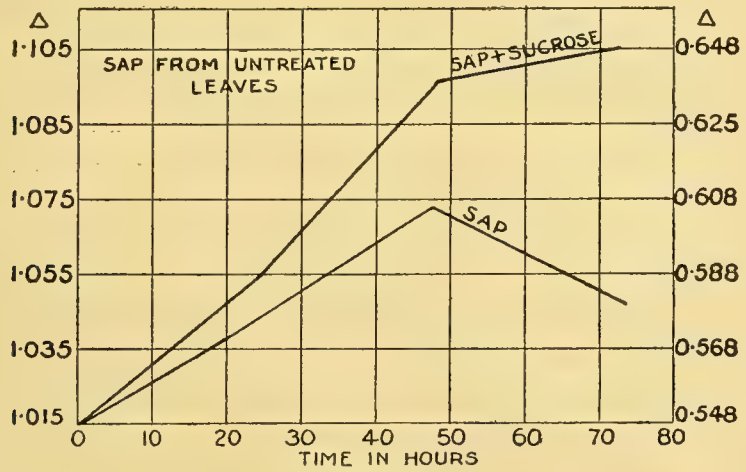

FIG. 3.

As the presence of inhibiting factors seemed to be a possible explanation of the observed depressions of the freezing-point, the saps (from the frozen and untreated leaves) were placed aside in the thermostat for a further forty-eight hours in order to see whether or not by then adding invertase the hydrolysis of sucrose was complete.

On withdrawing these saps (after 120 hours' incubation at 29°), they were boiled for one minute, as described in the second experiment.

To 5 gm. of the boiled and filtered saps was added 0·33 gm. of invertase solution, prepared by Davis' method (3). Before the addition of the invertase the saps were cooled to – 2° with a view to checking inversion till the freezing-points had been determined. When the observations were completed, the samples were stored for approximately twenty-four hours at 29°. The results are shown in Table VI.

For comparison, the freezing-points of the saps which had been boiled on the day of extraction, and to which 0·33 gm. of invertase had been added, are also shown. The increase in depression, corrected for dilution by the invertase added, is given in the last column.

TABLE VI.

Treatment.	Sap + 0·33 gm. Invertase solution.	Δ_0	Δ_{24}	$\Delta_{24} - \Delta_0$	$\Delta_{24} - \Delta_0$ corrected for Dilution
Frozen,	Sap boiled on day of extraction,	0·887°	0·958°	0·071°	0·075°
	Sap boiled after 120 hours' storage,	0·927°	0·964°	0·037°	0·039°
Untreated,	Sap boiled on day of extraction,	0·617°	0·661°	0·044°	0·047°
	Sap boiled after 120 hours' storage,	0·649°	0·663°	0·014°	0·015°

It will be observed that the inversion of the sucrose in the sap was not complete after 120 hours' storage at 29°.

It may be objected that a destruction of hexoses by respiratory enzymes would afford an explanation of the apparent inhibition of hydrolysis recorded in figures 1, 2, and 3. It must be admitted that such a view cannot be positively set aside; but the striking similarities in the freezing-points recorded under Δ_{24} of Table VI for the saps (to each of which ·33 gm. of invertase solution was added) which were boiled on the day of extraction, and in which the activity of all the enzymes was destroyed, to those in which the enzymes were not killed until a period of 120 hours had elapsed, do not point to such a destruction of sugar. If this destruction of hexoses by respiratory enzymes had taken place during storage in the saps which were not boiled on the day of extraction, it would presumably result in their showing a smaller depression of the freezing-point than that shown by the samples in which the enzymes were destroyed by boiling on the day the sap was extracted from the leaves. That this is not so, as the figures recorded under Δ_{24} in Table VI indicate, does not exclude the possibility of a destruction of hexoses, but renders it very improbable.

The interpretation of the decrease in depression shown in figs. 1 and 3 of the frozen and untreated saps is not clear; it is possibly due to a condensation of the hexoses of the sap to form sucrose. Robertson, Irvine, and Dobson (11) observed an association of this nature while working with sludges prepared from the leaves of *Beta vulgaris*. This condensation would, of course,

be masked by the greater velocity of hydrolysis in the initial stages of storage; but, with the introduction of factors limiting hydrolysis, a diminution in the depression of the freezing-point would be brought about.

In Table VII are shown the results obtained with a sample of sap pressed from leaves which had been exposed to toluene vapour for four hours. To 25 c.c. of this sap approximately 2 grams of invert sugar and sucrose respectively were dissolved.

These leaves were collected at 9.30 a.m. on April 22nd.

TABLE VII.

Description of Sample.	No. of Hours.						
	Δ_0	$\Delta_{4\frac{1}{4}}$	$\Delta_{7\frac{1}{2}}$	$\Delta_{11\frac{1}{2}}$	$\Delta_{24\frac{1}{2}}$	$\Delta_{31\frac{1}{2}}$	$\Delta_{42\frac{1}{4}}$
Hexose + Sap,	1·471°	1·469°	1·469°	1·475°	1·478°	1·485°	1·485°
Sucrose + Sap,	1·114°	1·119°	1·119°	1·123°	1·126°	1·136°	1·140°
Sap, . .	0·651°	0·651°	0.651°	0·652°	0·662°	0·662°	0·662°

This experiment does not call for comment, as it confirms the results of the last experiment.

There is no condensation of hexoses in the hexose-sap solution.

Bonns (2), in his work on etherization and enzyme activity, found that factors inhibiting the activity of invertase were introduced by exposure to ether vapour.

Possibly the slight decrease in the depression of freezing-point brought to light in these experiments may be attributed to the oxidation of hexoses.

In Table VIII are given the results of an experiment designed to determine if the sap pressed from material treated with toluene exerted an inhibiting influence on the invertase of yeast. To 50 c.c. of the sap 2 grams of sucrose were added.

The invertase solution was diluted with an equal volume of water, and evidently had much the same depression as the sucrose-sap solution, since its addition has produced only a very slight reduction in the depression. For comparison some of the sap was boiled before the addition of the invertase. In the last column is shown the increase in depression after storage at 29° for twenty-four hours.

TABLE VIII.

Description of Sample.	Δ_1	Δ_2	$\Delta_2 - \Delta_1$
Sap not boiled, 5 gm. No Invertase, . .	0·915°	0·916°	0·001°
Sap not boiled, 5 gm. + 1 drop Invertase, .	0·911°	1·158°	0·247°
Sap not boiled, 5 gm. + 3 drops Invertase, .	0·910°	1·164°	0·254°
Sap boiled, 5 gm. + 1 drop Invertase, . .	0·913°	1·140°	0·227°
Sap boiled, 5 gm. + 3 drops Invertase, .	0·910°	1·155°	0·245°

That the activity of the invertase added has not been limited is clear; this, though demonstrating that the negative results obtained with the sap are not associated with the production of substances of a toxic nature, yet does not indicate whether adsorption of the leaf enzyme, either before or after extraction of the sap, or its destruction is the cause.

As the factors inhibiting the activity of certain peroxidases have been removed by dialysing the sap (1), it was thought that similar treatment might possibly restore the activity of the enzyme in the sap pressed from toluened material. To 50 c.c. of the dialysed sap were added 2 gms. of sucrose; an equal weight of sucrose was also added to 25 c.c. of the same sap, which, however, had been stored for three days while dialysis was in progress in the first sample. The results are shown in Table IX; the results obtained with a sample of the sucrose-sap (not dialysed) diluted with an equal volume of water are also given.

TABLE IX.

Description of Sample.	Δ_1	Δ_2	$\Delta_2 - \Delta_1$
Dialysed Sap + Sucrose, ...	0·251°	0·259°	0·008°
Sap + Sucrose, ...	0·962°	0·977°	0·015°
Sap + Sucrose diluted with an equal vol. of water,	0·474°	0·484°	0·010°

The dialysis has evidently not been responsible for any increase in hydrolysis; it is possible that both enzyme and inhibitor diffused away.

In Table X are shown the changes in the depression of the freezing-point observed on incubating some sucrose and hexose solutions to which were added samples of sap pressed from leaves gathered at 4 p.m. and midnight respectively of April 7th. The tissues were rendered permeable by the freezing treatment; the sap was not filtered, but was stored in ice till the following morning. To 25 c.c. of the sap pressed from each sample were added 75 c.c. of a 6 per cent. sucrose and hexose (invert sugar) solution respectively. The solutions were kept saturated with toluene.

TABLE X.

Description of Sample.	Δ No. of Hours.							
	Δ_0	$\Delta_{2\frac{1}{2}}$	Δ_6	Δ_{10}	Δ_{34}	Δ_{41}	Δ_{56}	Δ_{52}
Day Sap + Sucrose solution,	0·447°	0·455°	0·454°	0·462°	0·476°	0·496°	0·514°	0·533°
Day Sap + Hexose solution,	0·654°	0·650°	0·650°	0·647°	0·662°	0·679°	0·690°	0·689°
Night Sap + Sucrose solution,	0·397°	0·417°	0·411°	0·410°	0·425°	0·441°	0·466°	0·479°
Night Sap + Hexose solution,	0·622°	0·622°	0·608°	0·611°	0·633°	0·646°	0·655°	0·655°

The depressions on the left and right of figures 4 and 5 refer to the hexose and sucrose samples respectively.

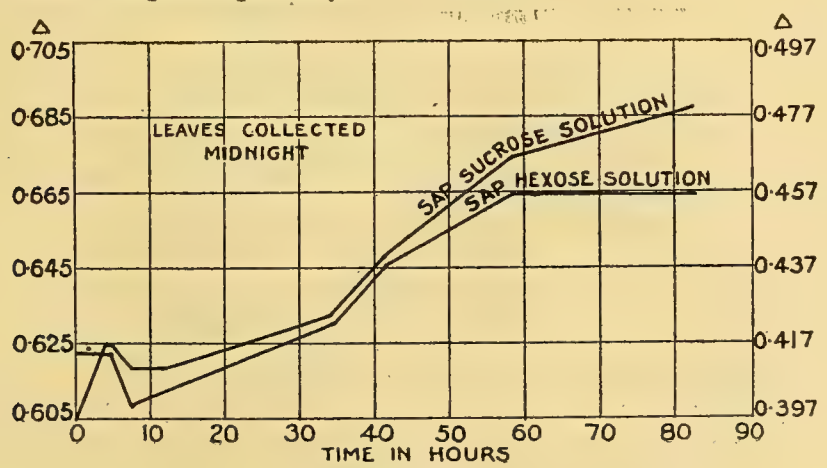

FIG. 4.

There is very little indication of any inhibition in the sucrose day sap, whereas there is a slight initial fall in the depression in that of the hexose

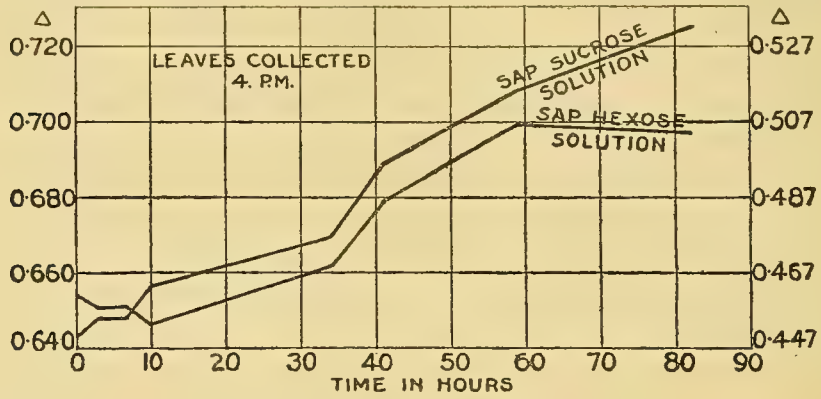

Fig. 5.

sample, due possibly to a condensation of the hexoses. The subsequent increase in the depressions of both samples, we are justified in assuming,

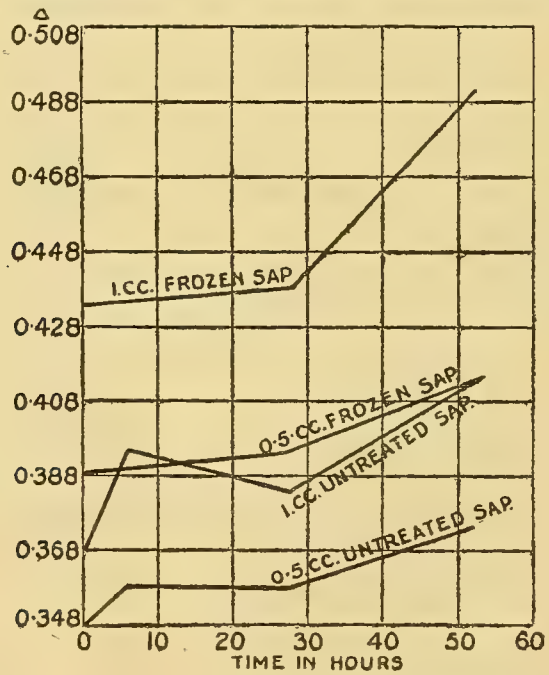

Fig. 6.

is due to the inversion of sucrose; that in the hexose sample is due to the inversion of the sucrose of the sap.

In both the night samples a condensation or destruction of hexoses is

indicated ; in the sucrose sample hydrolysis of sucrose is possibly masked by this condensation.

In the next experiment sap was pressed from leaves gathered at 9.30 a.m., March 25th. Saps pressed from both frozen and untreated leaves were used ; 1 c.c. and 0·5 c.c. respectively of each sample were added to 5 c.c. of a 6 per cent. sucrose solution. Toluene was not used.

TABLE XI.

Treatment.	Description of Sample.	Δ_0	$\Delta_{4\frac{3}{4}}$	Δ_{25}	Δ_{52}
Frozen,	1 c.c. of Sap + 5 c.c. Sucrose solution, ...	0·433°	0·434°	0·437°	0·491°
	0·5 c.c. of Sap + 5 c.c. Sucrose solution, ...	0·388°	0·390°	0·395°	0·415°
Untreated,	1 c.c. of Sap + 5 c.c. Sucrose solution, ...	0·368°	0·395°	0·386°	0·415°
	0·5 c.c. of Sap + 5 c.c. Sucrose solution, ...	0·348°	0·357°	0·358°	0·376°

The changes in depression of the sucrose sap solutions of the untreated leaves are somewhat similar to those of the night sucrose samples of fig. 4. In the frozen samples, however, the initial steep rise in depression is absent.

DISCUSSION.

The results obtained, though difficult to interpret, indicate that factors inhibiting the activity of the enzyme responsible for the hydrolysis of sucrose may be present in the sap. It has been pointed out that changes of a nature not yet understood (possibly, as Dr. Atkins has suggested to the writer, in the concentration of hydrogen ions) occur in the sap after its extraction from the leaf, which lead to a clumping of the colloids. It is suggested that the enzyme may be inactivated by adsorption on the coagulated colloids.

Thus the inactivity shown by the toluened sap would be due to the removal of the invertase by the precipitation of the colloids before the extraction of the sap from the leaf ; the absence of a colloid coagulum on storage supports this view. It is unnecessary to consider the factors which might lead to this

clumping of the colloids during the exposure of the leaves to the anæsthetic. It is not improbable, however, that it is associated with an increase in the concentration of the hydrogen ion as a result of the stimulation of respiration (12). In a similar way, the greater activity shown by the untreated sap (Table V) would be due to a partial precipitation of the colloids during the freezing of the leaves; as ice separates out in the cell vacuoles, the hydrogen ion becomes more concentrated, and will, as Harvey (8) has shown, bring about a precipitation of some of the colloids. The temperature to which the leaves are exposed must clearly be an important factor, according to this view, in determining the activity of the enzyme in the sap after its extraction.

The permanence of the inhibition would on this assumption depend on whether the colloid (anti-enzyme) on which the enzyme was removed was reversibly or irreversibly precipitated. It may be that the activity of the enzyme in the living cell is regulated by some such means.

It has been demonstrated by numerous investigators that sucrose accumulates in the assimilating cell during photosynthesis, and, as this accumulation of sucrose is of a very pronounced character, it is obvious that it cannot be stored in the presence of an enzyme actively engaged in bringing about its hydrolysis. It would follow, therefore, that either invertase is absent from the vacuoles where storage takes place, or else a mechanism is present whereby its activity is controlled; that the latter explanation is more probable is indicated by the experiments recorded in this paper.

Until such factors as temperature, traces of alkali dissolved from the glass, changes in the hydrogen ion concentration of the sap, and the effect of shaking have been considered, further discussion cannot be profitable.

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THE CHANGE IN THE RIGIDITY OF NICKEL WIRE WITH MAGNETIC FIELDS.

Smithsonian Institution
MAR 5 1921
National Museum

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VIII.

THE CHANGE IN THE RIGIDITY OF NICKEL WIRE WITH MAGNETIC FIELDS.

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Read June 22. Published August 9, 1920.

In March, 1917, one of us brought before this Society the results of some experiments on "The Change in Young's Modulus of Nickel with Magnetic Fields."[1] The present communication is a continuation of that work, and gives the results of some experiments on the change in the rigidity of nickel wires when subjected to the influence of magnetic fields, both longitudinal and transverse.

The change in the rigidity of nickel due to direct longitudinal magnetic fields, and under various loads, has been done by Honda and Terada;[2] but, as far as the present writers know, there have been no observations or measurements made on the effects of alternating longitudinal magnetic fields, or of direct and alternating transverse fields, and the present paper gives the results of some work with these types of magnetic fields.

The nickel wire used in the experiments was about 65 cms. long, 1·685 m.m. diameter, and of simple rigidity, 810×10^6 grammes per square cm.

A statical method of measurement was adopted, where the wire was arranged in a horizontal position, and firmly fixed at one end. On the other end there was fixed a light three-jaw clutch, which also supported a small light plane mirror, with its reflecting surface in the plane of the axis of the wire under test. On the end of this clutch there was a hook, to which was attached one end of a string of tortionless floss silk, the other end of this string being passed over a pulley, and attached to a scale-pan which carried the loads applied to the wire. The end of the nickel wire at the small clutch was supported on a horizontal piece of glass tubing, 2 m.m. in diameter,

[1] Scient. Proc. R.D.S., vol. xv, No. 20. [2] Phil. Mag., January, 1907, p. 36.

which was fixed on the top of a rigid stand. After a great many trials and preliminary experiments this arrangement was found to be practically frictionless and torsionless. The small clutch also carried an aluminium arm, consisting of a double sector of a circle of 4·5 cms. radius, which when 10 grammes weight were suspended from its circumference gave the initial torque to the wire under test.

The rigidity of the wire for a given torque varies inversely as the twist, and the changes in this twist due to the magnetic fields are what are recorded in the following tables and curves.

In order to observe and measure the change in the twist of the wire, a strong beam of light from a Nernst lamp was focussed on to the slit of a collimator, and after reflection from the mirror attached to the wire the image of the slit formed by the collimator lens was received in the eye-piece of a microscope reading to 0·001 cm. The distance of the collimator slit from the mirror was 56 cms., and the width of the slit was adjusted until diffraction bands were seen in the microscope; then a particular band was chosen as the line of reference in measuring the change in the twist. The distance from the mirror to the cross-hair in the microscope was 225 cms. so that a change in the twist of $\frac{100}{45} \times 10^{-6}$ radian, or 2·22 micro-radians, could be measured. The loads which were on the wire when being tested ranged from 10^5 to 4×10^5 grammes per square cm.; and the final results here recorded are in each case the mean of at least three different sets of measurements. The temperature of the room during the experiments was fairly constant, and did not vary more than half a degree above or below 15° C.

SECTION 1.

Longitudinal Magnetic Fields.

The solenoid used for this part of the work was 54 cms. long and 2·6 cms. internal diameter, and consisted of 2058 turns of double cotton-covered No. 18 copper wire in six layers, having a total resistance of 3·32 ohms. The strength of the magnetic field per ampere at the middle of the coil was 47·89 c.g.s. units, which for this work was taken as 48 units. There was no perceptible heating of the nickel wire under test when direct longitudinal magnetic fields were round it, but there was a slight heating when alternating magnetic fields were used. To eliminate, as far as possible, errors due to this heating, the observations were taken rapidly, and repeated many times, care being taken that the temperature of the room was kept constant, and an interval of time allowed to elapse between each set of readings.

The results for direct magnetic fields and for alternating fields of

frequencies 20, 50, and 100 per second are given in Table I, and two of the sets of observations are shown as curves in fig. 1.

TABLE I.

Load = 10^5 grammes per sq. cm.
Field H = 48 c.g.s. units per amp.

Amps.	Readings on microscope in cms. × 10^2.			
	D. C.	A. C.		
		$n = 20$	$n = 50$	$n = 100$
0·1	+ 0·75	+ 0·75	+ 0·75	+ 0·75
·2	+ 2·2	+ 2·0	+ 2·0	+ 2·7
·25		+ 4·0	+ 4·0	
·30	+ 4·4	+ 4·5	+ 5·5	+ 6·0
·34		+ 7·0	+ 7·5	+ 7·2
·36		+ 4·7	+ 7·5	
·38		− 1·2	+ 6·5	+ 7·7
·40	+ 7·8	− 7·5	+ 0·2	+ 6·0
·42		− 11·0	− 5·0	− 10·0
·45		− 15·0	− 12·5	− 19·0
·50	+ 13·5	− 18·0	− 20·0	− 26·3
·52	+ 14·5			
·54	+ 15·5			
·56	+ 14·5			
·58	+ 10·5			
·60	+ 1·5	− 21·5	− 25·5	− 32·0
·65	− 10·5			
·70	− 16·2	− 23·4	− 27·6	− 33·0
·80	− 20·0	− 23·6	− 28·5	− 32·5
·85	− 20·6		− 28·5	
·90	− 20·6	− 23·0	− 28·4	− 31·2
1·0	− 19·2	− 21·3	− 27·2	− 19·0
1·2	− 13·0	− 16·8	− 23·0	− 23·5
1·4	− 6·7	− 12·0	− 18·0	− 18·5
1·6	0	− 7·2	− 12·8	− 13·7
1·8	+ 6·0	− 2·5	− 8·0	− 9·2
2·0	+ 12·0	+ 2·4	− 3·4	− 5·0
2·5	+ 26·0	+ 14·2	+ 8·0	+ 4·7

From the table and the curves it will be seen that for a direct longitudinal field and given load on the wire the rigidity of nickel at first increases and reaches a maximum in a field of about 26 units; it then decreases rapidly to a minimum, which occurs in a field of about 41 units. It again increases up to its initial value in a field of about 77 units, and continues to further increase, as far as our observations went, that is, up to 120 units.

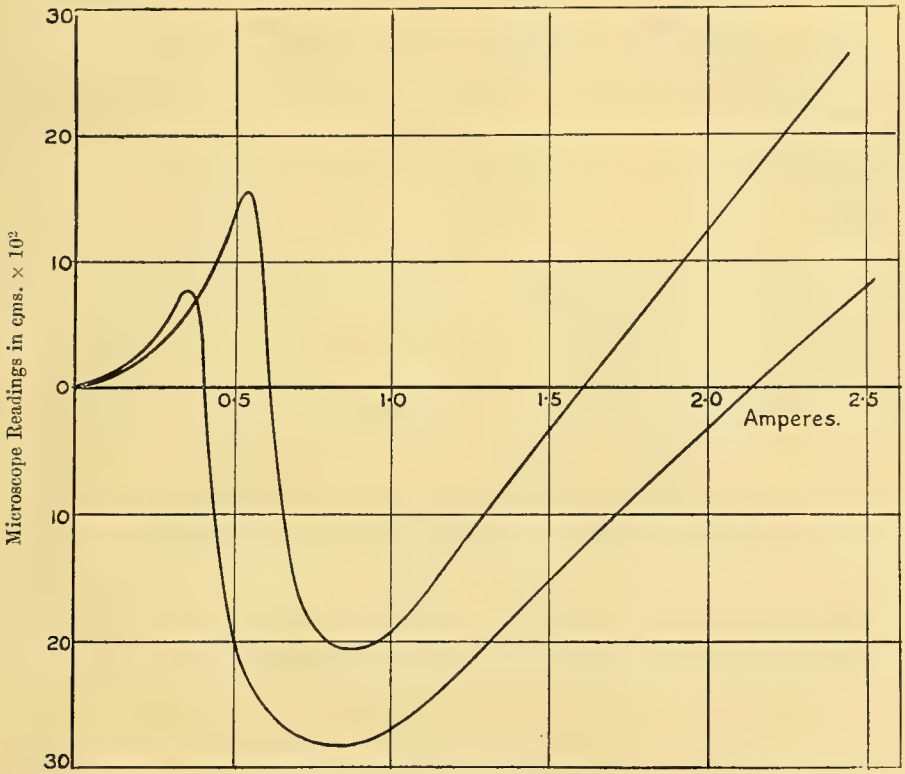

FIG. 1.—Upper Curve D. C. Field.
Lower Curve A. C. Field. (n = 50).

For the alternating longitudinal magnetic fields of frequency 50 per second, the curve follows the same general shape as with the direct field; but the first maximum is approximately half the value of the corresponding maximum for the direct field, and occurs in a magnetic field of about 17 units, whilst the minimum point is lower, and occurs in a field of about 38 units, then rises to its original value in a field of about 103 units. If the values in columns 3 and 5 of Table I (that is, for frequencies 20 and 100 per second) were plotted, the curves would be found to lie one above and one below the curve for frequency 50 per second.

One load only was tried in this part of the work, as the effect of increased

load has been shown by Honda and Terada in the paper already referred to above ; also the reason for repeating the measurements for direct longitudinal fields was that for the particular wire we used we should have a standard of comparison for the results obtained with the alternating longitudinal fields and the transverse fields.

SECTION 2.

Transverse Magnetic Fields.

In this part of the investigation the arrangement of the apparatus was the same as in the previous section, with the exception that the solenoid was replaced by a slotted iron tube. The transverse magnetic fields were produced in the air-gap of this soft iron tube by means of electric currents going through twenty-five copper wires running inside the tube. These copper wires of No. 8 s.w.g. were joined in series, and were well insulated from each other and from the iron tube.

The tube had a slot cut through the wall along its whole length of 51 cms. ; it was 4·8 cm. in external diameter, 4 cms. internal diameter, breadth of face of slot 0·4 cm., and width of slot 0·45 cm.

The magnetic field strength in the air-gap was measured in the usual way by means of an exploring coil and earth inductor, and was found to be 29·96, or, say, 30 c.g.s., units per ampere, that is, for one ampere in each wire there were 25 amperes flowing inside the iron tube to give a field of 30 units.

The loads on the wire used in this part of the work were from 2×10^5 to 4×10^5 grammes per sq. cm., so as to keep the wire stretched uniformly in the slot.

When the transverse magnetic fields were applied to the nickel wire it had a tendency to go towards one or other of the faces of the slot. In order to keep the wire in the centre of the slot and at the same time introduce as little friction as possible, small glass tubes 1·4 m.m. in diameter were placed vertically on each side of the wire at intervals of about 10 cms.

The slight friction introduced by these smooth tubes was overcome by gently tapping the iron tube before each reading of the microscope. The highest magnetic field obtainable without introducing errors due to heat was about 960 c.g.s. units, and up to this point the change in the twist of the wire gave no indication of reaching a maximum.

Before each set of measurements were taken the iron tube was carefully de-magnetized by putting through the wires inside it an alternating current of value equal to the maximum direct current used in the previous experiment, and gradually reducing it to zero. The tube was then allowed to rest for about half an hour, so that it should attain the temperature of the room before the next observations were made.

On account of the heating of the nickel wire under test by the alternating

magnetic field and the vibration of the mirror, we were not able to measure fully the effects of transverse alternating magnetic fields on the rigidity, but an approximate set of readings for fields of frequency 50 per second were obtained, which shows the general effect.

The results obtained are shown in Table II, and one set with direct fields, as well as the approximate values with the alternating fields, are shown as curves in fig. 2.

TABLE II.

Loads in grammes per sq. cm.

Field H = 30 c.g.s. units per amp.

	Readings on microscope in cms. × 10^2.			
Load. →	2×10^5	3×10^5	4×10^5	
Amps. ↓	D. C.	D. C.	D. C.	A. C.
0	0	0	0	0
2	− 0·75	+ 0·5	− 0·7	
4	+ 0·5	+ 1·5	− 1·0	+ 1·0
6	+ 2·7	+ 2·5	0	
8	+ 6·5	+ 4·7	+ 1·5	+ 2·5
10	+ 11·6	+ 7·1	+ 3·7	+ 3·5
14	+ 22·2	+ 14·6	+ 9·0	+ 6·5
18	+ 32·0	+ 22·2	+ 14·5	+ 10·0
20	+ 37·0	+ 26·5	+ 16·7	
22	+ 41·7	+ 30·4	+ 19·0	
24	+ 46·5	+ 34·0	+ 22·0	+ 15·5
26	+ 50·8	+ 38·0	+ 24·5	
28	+ 55·2	+ 44·0	+ 27·0	+ 18·0
30	+ 59·2	+ 45·7	+ 30·0	
32	+ 63·2	+ 49·5	+ 32·5	+ 21·0

From the values in Table II and the curves in fig. 2 it will be seen that the behaviour of nickel wire in transverse magnetic fields is the reverse of that in longitudinal magnetic fields—that is, there is at first a slight indication of a decrease in the rigidity—and that the main effect of the application of transverse fields, for the strongest fields that could be applied (960 units), is to increase the rigidity.

It is possible that for higher magnetic fields than the strongest here applied the curves may come to a maximum, then decrease, and cross the axis in the manner of those obtained with longitudinal fields. From the

approximate values we were able to obtain with alternating transverse fields it is evident that their action is the reverse of that for alternating longitudinal fields, where the changes in the rigidity were greater than for direct longitudinal fields, whereas the changes for alternating transverse fields are less than for direct transverse fields.

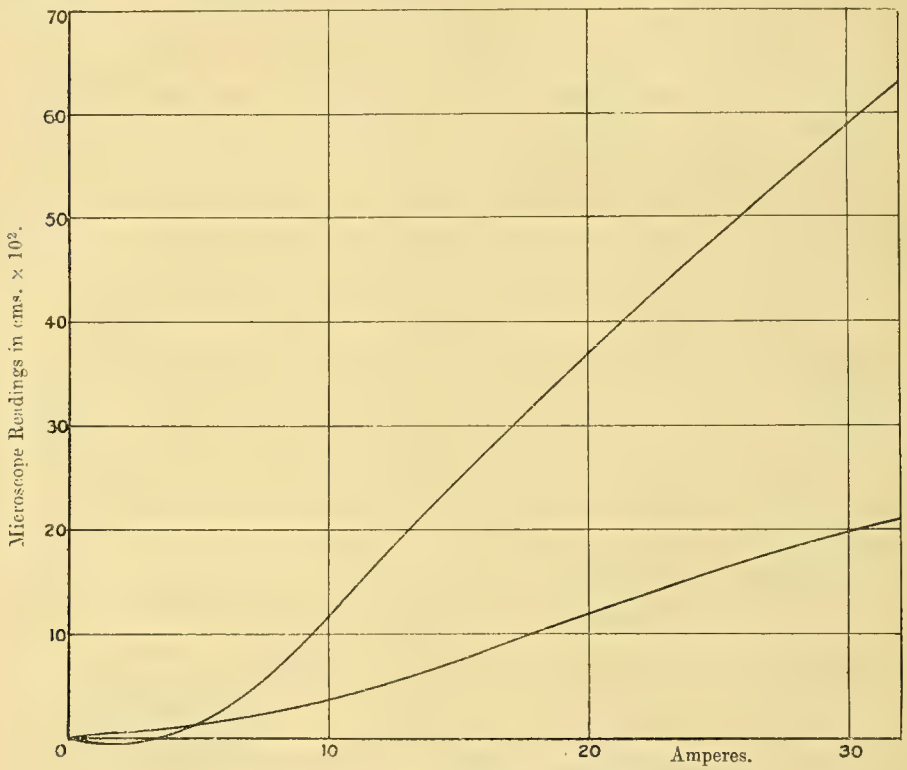

Fig. 2.—Upper Curve D. C. Field. Load 2×10^5 grm./cm².
Lower Curve A. C. Field ($n = 50$). Load 4×10^5 grm./cm².

In conclusion, it may be said :—

1. The initial increase in the rigidity of nickel is less for alternating than for direct longitudinal magnetic fields, whilst the subsequent decrease is greater for alternating longitudinal fields than for direct fields.

2. The higher the frequency of the longitudinal magnetic field used the greater the decrease in the rigidity.

3. The changes in the rigidity of nickel wire with transverse magnetic fields are the reverse of those due to longitudinal fields, both direct and alternating.

4. The greater the load on the wire, when subjected to transverse magnetic fields, the smaller the change in the rigidity for fields between zero and 960 units.

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THE

SCIENTIFIC PROCEEDINGS

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SOME DERIVATIVES OF NITROTOLUIDINE

(4-nitro-2-amido-1-methyl-benzene).

BY

A. G. G. LEONARD, A.R.C.Sc.I., B.Sc., PH.D.;

AND

AGNES BROWNE, A.R.C.Sc.I., B.Sc.

Smithsonian Institution
MAR 5 1921
National Museum

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MAR 5 1921
National Museum

IX.

SOME DERIVATIVES OF NITROTOLUIDINE (4-nitro-2-amido-1-methyl-benzene).

By A. G. G. LEONARD, A.R.C.Sc.I., B.Sc., Ph.D.;
AND
AGNES BROWNE, A.R.C.Sc.I., B.Sc.

Read June 22. Published August 10, 1920.

The nitro-ortho-toluidine $C_6H_3(NH_2)Me(NO_2)$ [$NH_2 : Me : NO_2 = 1 : 2 : 5$] used for the following preparations was obtained by nitration of *o*-toluidine in excess of sulphuric acid (Nölting and Stoecklin, Ber. **24**, 566). Three lots of 100 grams of the base gave an average yield of 83 grams of nitro-toluidine, m. pt. 107° C.

Nitro-methyl-phenylazo-β-Naphthol, $C_6H_3Me . NO_2 . N_2 . C_{10}H_6 . OH$
(2.) (5.) (1,1.) (2.)

5 grams nitro-ortho-toluidine were dissolved in 75 c.c. warm sulphuric acid (10%), and the solution rapidly cooled to 0° C., whereby the sulphate was precipitated in a fine state of division. A cold solution of 2·27 gram sodium nitrate was added slowly, the diazo solution quickly filtered and added with constant stirring to a cold solution of 4·74 grams of β-naphthol in 500 c.c. of a 3% solution of sodium hydroxide. During the mixing of the liquids a bright red precipitate separated. Stirring was continued for an hour, when the whole was heated to 80° C. on the water bath, cooled, filtered, and the precipitate washed with water. Yield, 9·5 grams.

The product thus obtained was bright red, and melted with decomposition at 204° C. It is insoluble in water, hydrochloric acid, and sodium hydroxide; it dissolves in benzene, ether, and alcohol, and crystallizes from its solution in alcohol in long red needles.

When applied to the fibre in the same way as *p*-nitraniline red, it dyes cotton a deep orange colour.

Analysis :—

(1) ·2997 gram gave 33·6 c.c. moist nitrogen at 17° C. and 785 mm.
% N = 13·42.

(2) ·3008 gram gave 34·4 c.c. moist nitrogen at 18° C. and 765 mm.
% N = 13·30.

$C_{17}H_{13}O_3N_3$ requires 13·68.

Nitro-methyl-benzene-diazo-amino-o-toluene $C_6H_3 . NO_2 . Me . N_2 . NH . C_6H_4 . Me.$
(5) (2) (1) (1) (2)

7·6 grams of nitro-toluidine were dissolved by warming with 50 c.c. conc. hydrochloric acid diluted with an equal volume of water. The solution was quickly cooled in ice, and the requisite quantity of sodium nitrite solution added. The diazo solution was rapidly filtered, diluted to 250 c.c., and excess of sodium acetate added. 5·35 grams of *o*-toluidine were dissolved in 30 c.c. conc. hydrochloric acid and 50 c.c. water; the solution was diluted to 500 c.c., and excess of sodium acetate added. This solution was then cooled and added to the diazo solution previously prepared, when an orange yellow precipitate separated gradually. The substance was filtered off after standing overnight and well washed with water. The crude product melted at 108° C., but after four crystallizations from alcohol the melting point rose to 133° C. The substance so obtained consisted of needle-shaped crystals, which decomposed on boiling with hydrochloric, sulphuric, and acetic acids, giving nitro-cresol [OH : Me : NO_2 = 1 : 2 : 6], *o*-toluidine, and nitrogen, thus showing it to be a diazo-amino compound. Again, on heating with hydrochloric acid and β-naphthol it yielded nitro-methyl-phenyl-azo-β-naphthol m.pt. 204° C.; it was found that about 12% of the diazo-amino product reacts in this manner, the remainder yielding nitro-cresol, toluidine, and nitrogen.

Analysis :—

·1500 gram gave 25·8 c.c. moist nitrogen at 12° C. and 772 mm.
% N = 20·86.

$C_{14}H_{14}N_4O_2$ requires 20·74.

The "diazo" nitrogen was estimated by the method of Mehner (Journ. für Prakt. Chemie [2], 63, 304).

·3000 gram gave 28 c.c. moist nitrogen at 20° C. and 764 mm.
% diazo nitrogen = 10·76.

$C_6H_3NO_2 . Me . N : N . NH . C_6H_4Me$ requires 10·37.

On concentration of the mother liquor from the crystallization of the above compound a small quantity of reddish crystals separated. This was picked out and crystallized from alcohol, m.pt. 144° C. Under the microscope the crystals were seen to be cubic. The amount of the substance was too small for analysis; it was probably the isomeric 4-amino-3 : 2′-dimethyl-5-nitro-azo-benzene.

Nitro-methyl-benzene-diazo-amino-p-toluene $C_6H_3NO_2 . Me . N_2 . NH . C_6H_4 . Me.$
(5) (2) (1) (1) (4)

1·52 gram nitro-toluidine was dissolved in 4 c.c. conc. hydrochloric acid and 50 c.c. water, cooled to 0° C., diazotized with the requisite quantity of

sodium nitrite solution, the whole filtered, and excess of sodium acetate added. The clear solution was added slowly to a solution of 1·07 gram *p*-toluidine in 4 c.c. conc. hydrochloric acid and 200 c.c. water containing excess of sodium acetate. A yellow substance gradually separated, which was filtered off after standing overnight. Twice crystallized from alcohol, the crystals melted with decomposition at 131° C. It proved on examination to be a diazo amino compound, decomposing on treatment with acids into nitro-cresol, *p*-toluidine, and nitrogen.

Analysis :—

·1500 gram gave 25·8 c.c. moist nitrogen at 14·5° C. and 767 mm.

% Nitrogen = 20·50.

$C_{14}H_{14}N_4O_2$ requires 20·74.

Diazo nitrogen :—

·3000 grams gave 27·8 c.c. moist nitrogen at 20° C. and 767 mm.

% Diazo nitrogen 10·33.

$C_6H_3NO_2$. Me . N : N . NH . C_6H_4 . Me requires 10·37.

Nitro-methyl-diazo-aminobenzene-p-sulphonic acid

$$C_6H_3 . \underset{(5)}{NO_2} . \underset{(2)}{Me} . \underset{(1)}{N_2} . \underset{(1)}{NH} . C_6H_4 . \underset{(4)}{SO_3H}.$$

$\frac{1}{60}$th molecule of nitro-o-toluidine dissolved in 75 c.c. of 10 % sulphuric acid and cooled to 0° C. was diazotized by $\frac{1}{60}$th mol. of sodium nitrite. The solution was then added with constant stirring to a solution of $\frac{1}{60}$th mol. of sulphanilic acid in 100 c.c. of a solution containing $\frac{1}{60}$th mol. of sodium hydroxide.

After a short time a yellow amorphous substance separated, which, after washing and drying in vacuo, melted at 129° C. with decomposition. It is insoluble in water, alcohol, ether, and benzene in the cold, and only slightly soluble on heating. When warmed with acids it decomposes with evolution of nitrogen, showing it to be a diazo-amino compound.

Analysis :—

·3000 gram gave 43·2 c.c. moist nitrogen at 16° C. and 752 mm.

% nitrogen = 16·71.

$C_{13}H_{12}N_4SO_5$ requires 16·67.

Diazo nitrogen :—

·3000 gram gave 21 c.c. moist nitrogen at 17° C. and 761 mm.

% diazo nitrogen = 8·19.

$C_6H_3 . NO_2 . Me . N : N . NH . C_6H_4SO_3H$ requires 8·33.

Methyl-nitrodiazoamino-p-nitrobenzene $C_6H_3 . NO_2 . Me . N : N . NH\ C_6H_4 . NO_2$.
(5) (2) (1) (1) (4)

$\frac{1}{60}$th mol. of nitrotoluidine dissolved in sulphuric acid and diazotized as before was added with constant stirring to $\frac{1}{60}$th mol. of *p*-nitraniline in 75 c.c. of 10% sulphuric acid, the whole being kept at 0° C. On standing overnight a yellow substance separated, which was filtered off, washed and dried in vacuo.

It dissolves in warm alcohol, but is insoluble in ether and benzene. It melts with decomposition at 118° C. It is decomposed by boiling with acids with evolution of nitrogen, showing it to be a diazo animo compound.

Analysis :—

(i) ·1500 gram gave 30·0 c.c. of moist nitrogen at 19° C. and 762 mm.

(ii) ·1500 gram gave 29·6 c.c. of moist nitrogen at 17° C. and 767 mm.

% nitrogen = 23·23 and 23·27.

$C_{13}H_{11}N_3O_4$ requires 23·25.

Diazo nitrogen :—

·3000 grams gave 22·4 c.c. moist nitrogen at 18° C. and 764 mm.

% diazo nitrogen = 8·87.

$C_6H_3NO_2 . Me . N : N . NH . C_6H_4 . NO_2$ requires 9·30.

2-Methyl-5-nitro-2′ : 4′-dihydroxyazobenzene $CH_3 . NO_2 . C_6H_3 . N_2 . C_6H_3 . (OH)_2$.
(2) (5) (1,1) (2, 4)

$\frac{1}{100}$th mol. of nitrotoluidine was diazotized in hydrochloric acid solution as before, and the solution added to a cold solution of resorcinol ($\frac{1}{100}$th mol.) in 50 c.c. water. After stirring for a short time a bright red gelatinous precipitate separated, which after two or three hours became orange in colour. The precipitate was allowed to stand overnight and was then filtered off, washed, and dried in vacuo. The product is fairly soluble in hot alcohol, and separates out on cooling in an amorphous condition. It is only sparingly soluble in benzene and petroleum ether. Melting point, 234° C.

Analysis :—

·2500 gram gave 31·8 c.c. moist nitrogen at 13° C. and 768 mm.

% nitrogen = 15·29.

$C_{13}H_{11}N_3O_4$ requires 15·38.

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AN INVESTIGATION INTO THE CAUSES OF THE SELF-IGNITION OF ETHER-AIR MIXTURES.

BY

THE LATE PROF. J. A. McCLELLAND, D.Sc., F.R.S.,

AND

REV. H. V. GILL, S.J., D.S.O., M.C., M.A.

(UNIVERSITY COLLEGE, DUBLIN).

Smithsonian Institution
MAR 5 1921

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National Museum

X.

AN INVESTIGATION INTO THE CAUSES OF THE SELF-IGNITION OF ETHER-AIR MIXTURES.

By the late PROF. J. A. McCLELLAND, D.Sc., F.R.S.,
AND
REV. H. V. GILL, S.J., D.S.O., M.C., M.A.
(University College, Dublin).

[Read June 22. Published August 13, 1920.]

The investigation described in this paper arose out of an inquiry into conditions under which mixtures of ether and other substances with air ignite. In the course of work on this subject, carried out for Messrs. Nobel's Explosives Co., Ltd., by Messrs. White and Price (Journ. Chem. Soc., December, 1919, p. 1462), it was noticed that a mixture of air and ether ignited under the conditions described in the present paper. A preliminary examination of this phenomenon was made by these workers, who, however, did not continue their experiments. The results of our preliminary examination, described in Section A, agree with their results. The conclusion arrived at by White and Price is that "the information at present available makes it appear highly probable that the ignition is due to shock caused by the sudden stoppage of the gas rushing into the exhausted tube."

The object of the investigation here described was to elucidate further the principles underlying this "shock" ignition, which is evidently a fact of the greatest importance from many points of view.[1]

The apparatus with which we first studied the effect was as follows:—R (fig. 1) is a reservoir of about 10 gallons capacity. It is connected by a glass tube, C.T., 30 inches long and 1-inch diameter, with a wider tube, Ex.T., 3 feet long and 3 inches in diameter. It was in this wider tube that the explosion occurred when the mixture was allowed to rush through the tap T

[1] Professor M'Clelland was invited by Messrs. Nobel's Explosives Co. to undertake this work, and this paper gives an account of the work done and the results arrived at in conjunction with him. Although it was completed and typed before the lamented death of Professor M'Clelland, it is right to state that it has been necessary to prepare it for publication in its present form without the benefit of his advice. I wish to thank Messrs. Nobel's Explosives Co. and Mr. W. Rintoul, Manager of the Research Section, for kind permission to publish our results.—H.V.G.

(of about 2 sq. cm. aperture) from the reservoir into the partially exhausted tubes. In carrying out an experiment, the reservoir was exhausted to about half an atmosphere; 10 c.c. of ether were then allowed to enter along with air to restore the pressure to that of the atmosphere. The wide tube, Ex.T., together with the connecting tube, were then exhausted to the pressure of a few cm. of mercury. The tap T was then turned quickly, so as to allow a sudden rush of the air-ether mixture into the exhausted tubes. In the initial experiments the tap was turned by hand, but afterwards an arm was attached to the tap, and arranged to be rapidly rotated by a strong spring on releasing a trigger. This ensured that in different experiments the tap was opened at approximately the same rate. When the expansion took place, a blue flame was observed to start at the end of the wide tube remote from the reservoir; this flame travelled up the wide tube and sometimes developed into an explosion strong enough to blow the tubes apart, and even at times to shatter them.

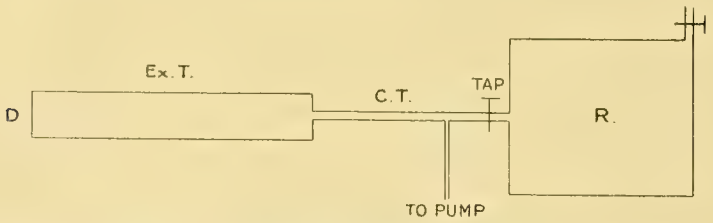


Fig. 1.—Showing the apparatus with which the effects connected with the sudden expansion of a mixture of air and ether were first studied.

We found it convenient to join up the apparatus with rubber corks and plasticine, and the end D of the wide tube was usually closed with a glass or metal plate fastened on with plasticine. In this way it was easy to repeat the observations quickly, and to avoid having the apparatus broken when explosions occurred.

The flame often travelled down the wide tube without any explosion taking place. Again, when the conditions were not such as to produce a visible flame, the smell of the gas remaining in the tube after the experiment often indicated that slight combustion had taken place. Sometimes the flame passed into the connecting tube, and in repeating the experiment it is prudent to close the tap T as soon as ignition has been observed, in order to avoid a serious explosion by the ignition of the ether-air mixture in the reservoir.

The investigation into the nature and cause of these ignition effects may be described under three headings:—

A. Experiments with ether-air mixtures expanding into glass tubes, in order to study the phenomenon generally.

B. Experiments with air or other gas without ether vapour with the object of determining the distribution of temperatures by means of a thermo-couple at different parts of the apparatus.

C. A determination of the actual temperature reached by air under the conditions of the ether-air experiments.

A.—*General Effects Observed.*

Provided that there was a sufficient quantity of ether present, the exact proportions of air and ether in the reservoir did not appear to be of importance. The ordinary ether supplied to the laboratory was used without any special purification. The humidity of the mixture did not appear to interfere with the result of the experiments. Explosions were obtained both when the reservoir was perfectly dry and when it had just been washed with water inside. The presence of dust had apparently no special significance.

The pressure of the mixture in the reservoir could be varied between fairly wide limits without interfering with the result of the experiments. In our experiments the pressure was usually atmospheric.

The influence of the pressure of the residual air in the exhausted explosion-tube was studied in some detail. Ignition was obtained at the lowest pressures possible in our apparatus. When the pressure exceeded 5 cm. of mercury, no ignition was observed. The most suitable pressure seemed to be about 3 or 4 cm. in the explosion-tube when the pressure of the mixture in the reservoir was atmospheric. Considerable difficulty was experienced in obtaining very low pressures in the explosion-tube, as it was difficult to obtain a large tap which was at the same time perfectly air-tight. By employing the following device, a low pressure was obtained:—Two large taps, as air-tight as possible, were joined in series, with a short space between them. The tap near the explosion-tube was surrounded by a bath of thick oil, so that no leak could take place into the explosion-tube except through the space between the taps. This space was kept exhausted by means of an air-pump until just before the experiment, when the tap near the reservoir was opened. By this means, using a mercury air-pump, the pressure in the explosion-tube was reduced as low as 0·008 mm.

The length of the connecting tube did not seem to have any marked influence on the ignition. Tubes of varying lengths were employed with success. It is prudent to have the tube of sufficient length to ensure that the flame will not reach the reservoir.

The length of the explosion-tube is a matter of importance. Ignitions or explosions were obtained in tubes varying from somewhat less than three feet to eight feet. Longer tubes would probably have served as well.

No explosion or ignition was observed in tubes less than about two feet long. The diameters of tubes in which the effect was observed varied from two to somewhat more than three inches. Tubes of about one inch in diameter were not suitable.

The nature of the end of the explosion where the ignition began had a marked effect on the result of experiments. A pad of cotton wool, about an inch and a half thick, prevented ignition. A bulb, three inches in diameter, was fixed into a hole of the end plate of the explosion-tube. The flame began in the bulb, but did not travel up the tube. The explosion-tube was replaced by a bell-jar of about ten inches diameter, and having approximately the same volume as the tube, but no ignition was obtained in the jar.

Experiments were made to find out what effect the presence of obstacles in the explosion-tube might exert. Ignition took place when a pad of wire gauze, up to six layers thick, was placed across the middle of the tube. A pad ten layers thick prevented ignition.

B.—*Temperature Experiments.*

As the cause of the ignition seemed to be due to the heating of the ether-air mixture, it seemed useful to examine the rise in temperature of pure air when used in the place of ether-air mixtures. The conditions under which these experiments were made were identical with those in the case of the experiments described.

Small pieces of phosphorus fixed axially in the explosion-tube were ignited at distances from the closed end varying from a few millimeters to a few centimeters. At distances greater than about 5 cm. the phosphorus was not ignited.

Experiments were then undertaken with the object of studying the distribution of temperatures in the different parts of the explosion-tube by means of a thermo-couple. The thermo-junction consisted of thin copper and constantan wires soldered together and to thicker leads of the same materials. The leads passed through a glass tube, which, in turn, passed through a small metal tube fixed on to the metal disc closing the end of the tube. By means of a clamp the junction could be placed at any required distance from the end of the tube. The aperture through which the tube passed was kept air-tight by means of plasticine. In all cases the junction was placed axially in the tube. The numbers on which the curves are drawn refer to the deflections of a ballistic galvanometer in series with the couple. The swing was reduced by putting resistances of from 500 to 700 ohms in series with the galvanometer. The different curves serve to indicate the

temperatures developed at the various positions indicated. In each series the numbers arrived at are the means of several observations. The agreement between successive observations taken under apparently identical conditions was not very exact. The tap may not have been always opened in exactly the same manner. The strong rush of air down the wide tube may also have affected the delicate thermo-junction. It was impossible to obviate this possibility.

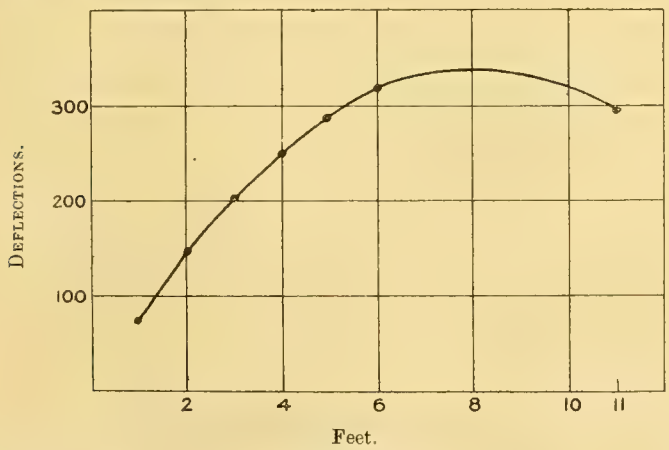
Table I.

Relation between the galvanometer deflection and the length of the explosion-tube :—

Initial pressure of air in explosion-tube, . . 2 cm.
Distance of junction from end of tube, . . 2·5 cm.
Diameter of tubes, ... 7·5 cm.
Pressure in reservoir, ... atmospheric.

Length of explosion-tube.	Deflection of galvanometer.
1 ft.	74
2 „	147
3 „	202
4 „	245
5 „	287
6 „	310
11 „	295

Thus the temperature produced increased in tubes up to 6 feet long, but had decreased for a length of 11 feet. It was not convenient to use tubes between 6 and 11 feet long.



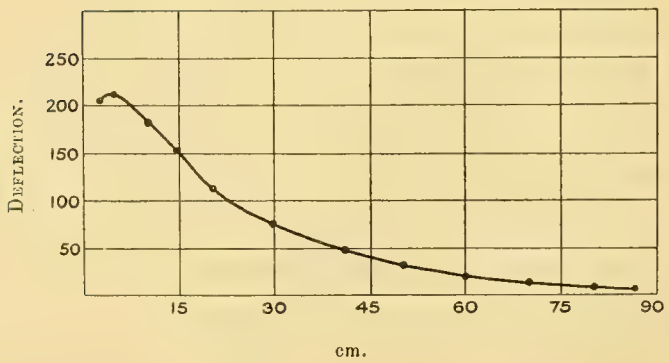
Curve 1.—Showing relation between deflections and length of explosion-tube.

TABLE II.

Relation between the distance of junction from the closed end and the galvanometer deflection :—

(*a*) Length of explosion-tube, ... 3 ft.
Diameter of tube, ... 3 in.
Initial pressure of air in tube, . . . 2 cm.
Pressure in reservoir, ... atmospheric.

Distance of junction from end of tube.	Deflection of galvanometer.
2·5 cm.	202
5·0 „	205
10·0 „	180
15·0 „	154
20 0 „	111
30·0 „	76
40·0 „	50
50·0 „	32
60·0 „	19
70·0 „	13
80·0 „	7
85·0 „	6

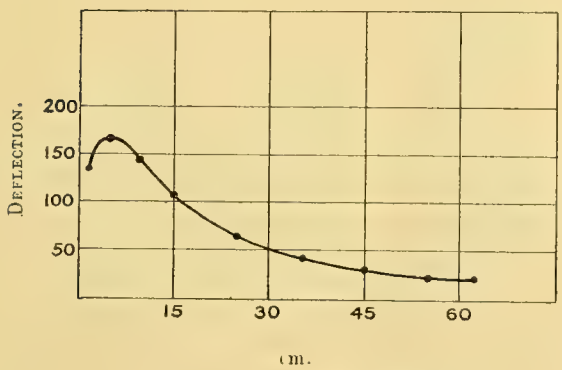


CURVE 2*a*.—Showing relation between deflection and distance of junction from closed end of explosion-tube. Tube 3 feet long.

Table III.

(*b*) Length of explosion-tube, ... 2 ft.
Diameter of tube, ... 3 in.
Initial pressure of air in tube, ... 2 cm.
Pressure in reservoir, ... atmospheric.

Distance of junction from end of tube.	Deflection of galvanometer.
1·5 cm.	135
5·0 „	166
10·0 „	146
15·0 „	102
25·0 „	66
35·0 „	41
45·0 „	32
55·0	23



Curve 2*b*.—Showing relation between galvanometer deflection and distance of junction from closed end of explosion-tube. Tube 2 feet long.

In all cases where the junction was very near the disc closing the explosion-tube, the temperature as indicated by the deflection of the galvanometer fell off. This falling-off was, no doubt, due, in part at least, to the cooling effect of the neighbouring metal disc.

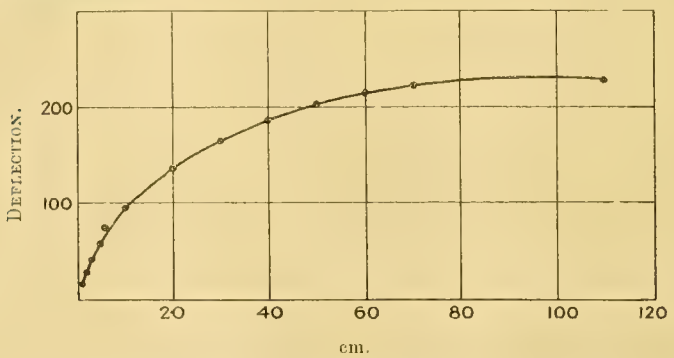
TABLE IV.

Relation between pressure difference in reservoir and explosion-tubes and galvanometer deflection:—

Length of explosion-tube, ... 3 ft.
Diameter of explosion-tube, ... 3 in.
Distance of junction from end, . . . 1 in.
Initial pressure in tube, ... 2 cm.
Pressure in reservoir varied.

Difference of pressure in reservoir and tube.	Deflection of galvanometer.
1 cm.	15
2 „	24·5
3 „	39
4 „	57
5 „	75
10 „	95
20 „	135
30 „	160
40 „	182
50 „	200
60 „	215
70 „	225
115 „	230

For the last reading the pressure of air in the reservoir was increased by means of a force-pump.



DIFFERENCE OF PRESSURE BETWEEN RESERVOIR AND TUBE.

CURVE 3.—Showing relation between pressure difference in reservoir and explosion-tube and galvanometer deflection.

An experiment was made to determine the effect of placing a pad of cotton wool at the end of the tube. In the first experiment the junction was 8 cm. from the end of the tube. The pad was about 3 cm. thick. The pressure of air in the tube was 2 cm. The length of the tube was 3 feet, and the diameter 3 inches.

Without pad, . . . Deflection, 151.
With pad, . . . „ 110.

In the second experiment the pad was not so thick, and the junction was placed quite near it. The other conditions were the same.

Without pad, . . . Deflection, 155.
With pad, . . . „ 143.

In both cases there was apparently a diminution of temperature, which agrees with the result already described as to absence of ignition of an ether-air mixture under the same conditions.

The part played by the connecting tube was also tested by this method. The tube usually employed was 30 inches long. This was replaced by a tube only 2 inches long. In experiments carried out under similar conditions, except for the lengths of the connecting tubes, there was no appreciable difference in the deflections due to the thermo-couple. This result was to be expected from the conclusions already arrived at.

C.—*Actual temperature reached by the air in the above experiments.*

The numbers given above, expressed in terms of the galvanometer deflections, merely indicate the relative values of the temperature. To find the actual temperature reached we employed the following method :—

A, B (fig. 2) represents a potentiometer through which a current can be sent from the cell E when the key K is closed. G is a galvanometer and J the thermal-junction mounted inside the tube into which the air is allowed to rush. M is an electro-magnet, from which the wires (*a* and *b*) are taken to the point where the spring and lever arrangement opens the tap, allowing the air to rush from the reservoir. It is arranged that the lever opens the electro-magnet circuit, and consequently the galvanometer circuit closes at D. The contact C is varied, so that the potentiometer electromotive force balances the electromotive force of the thermal-junction. The potentiometer e.m.f. can be varied, so that the slight sudden kick of the galvanometer is in either direction when the tap is opened. Of course, the junction very soon begins to cool, and then the galvanometer moves in the direction corresponding to the e.m.f. of the potentiometer. The exact instant of closing the galvanometer circuit could be varied relatively to the time of opening the tap, and in

this way the maximum temperature reached by the thermal-junction could be found.

A careful determination of the maximum temperature was made in this way when the junction was placed 2·5 cm. from the end of the explosion-tube 3 feet long and 3 inches in diameter. The pressure of the air in the tube was 2 cm., that of the air in the reservoir being atmospheric. About 3 feet is the shortest length of explosion-tube which was certain to give good ignition. The junction was carefully calibrated over the range indicated by the galvanometer deflections.

The temperature reached by the air under these conditions varied between 185° and 193° C.

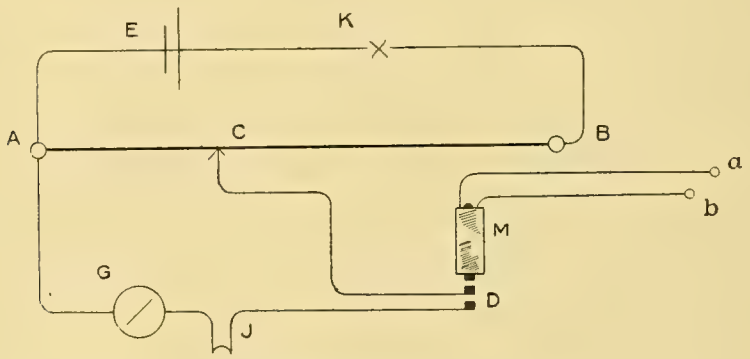


Fig. 2.—Potentiometer arrangement by means of which the actual temperature reached in the explosion-tube was determined.

From the results of the various temperature determinations we made, it may be concluded that at a short distance from the closed end of the explosion-tube, 3 feet long, a temperature as high as 190° C. may occur when air at atmospheric pressure is allowed to rush in, the pressure of the residual air in the tube being about 2 cm. of mercury. From our earlier experiments it would follow that higher temperatures would be reached with longer explosion-tubes.

Assuming that when air is replaced by an ether-air mixture the temperature reached is not very different, we have to consider whether this rise of temperature is sufficient to ignite the mixture.

M. E. Alilaire (Comptes Rendus, tome clxviii, No. 14, Avril, 1919, p. 729) has recently studied the ignition of ether-air mixtures, and has found it possible to produce ignition at a temperature of 190° C. He states that with modifications of his apparatus he is of opinion that ignition could be obtained at even lower temperatures. The agreement is close between the lowest

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THE INFLUENCE OF ELECTROLYTIC DISSOCIATION ON THE DISTILLATION IN STEAM OF THE VOLATILE FATTY ACIDS.

BY

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AND

WILFRED J. HICKINBOTTOM, B.Sc.

[COMMUNICATED BY DR. F. E. HACKETT, M.A.]

Smithsonian Institution
MAR 5 1921
National Museum

[Authors alone are responsible for all opinions expressed in their Communications.]

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ignition temperature found by Alilaire and the temperature we measure in the shortest tube in which we found it most satisfactory to obtain ignition.

Discussion of Results.

1. With the type of apparatus employed we have found that when the explosion-tube is about 3 feet in length, or longer, a temperature of 190° C., or higher, may occur near the end of the tube. It has been found (Alilaire) by other methods that a temperature of 190° C. is sufficient to ignite an ether-air mixture. We may therefore conclude that the ignition observed in these experiments is simply due to the rise of temperature produced.

2. We may now consider how the high temperature is produced in the explosion-tube, the distribution of temperature along the tube, and the way the temperature produced depends on the dimensions of the apparatus. When the tap is opened the inrush of air, etc., from the reservoir reaches a high velocity, approximately equal to the velocity of sound. A stream of gas travels down to the further end of the explosion-tube, and the reflected stream meets the direct stream, with the result that the translational energy is quickly changed into heat, the maximum generation of heat taking place near the closed end of the tube. We can from these considerations understand the distribution of temperature along the tube as shown on the curves.

MAR 5 1921

The effect of the plug of cotton wool at the end of the tube in preventing ignition results from the way it militates against the formation of the reflected stream. The influence of the pressure of the residual gas in the tube before the inrush takes place is also clear. The pressure in the explosion-tube might be varied considerably without having much influence on the velocity of efflux from the reservoir; but, on the other hand, an increase of the amount of gas in the tube would cause the heat produced when the velocity of the stream of inrushing gas is destroyed to be more evenly distributed along the tube. It is not clear why the temperature generated near the further end of the explosion-tube depends to such an extent on the length of the tube. With the apparatus described, ignition does not take place unless the explosion-tube is at least about 3 feet in length; and curve 1 shows how different is the maximum temperature in the air experiments when the length of the tube is increased to 6 feet or more. The velocity of the inrushing stream will increase to some extent when it enters and travels down the wide tube; the fall of pressure in the jet will be accompanied by an increase of velocity. Whether this is the only factor accounting for the effect due to the length of the explosion-tube is a matter worthy of further consideration. Further work in this and other points of interest is in contemplation. These experiments were carried out in the Laboratory of University College, Dublin.

XI.

THE INFLUENCE OF ELECTROLYTIC DISSOCIATION ON THE DISTILLATION IN STEAM OF THE VOLATILE FATTY ACIDS.

By JOSEPH REILLY, M.A., D.Sc., F.R.C.Sc.I.,

AND

WILFRED J. HICKINBOTTOM, B.Sc.

[COMMUNICATED BY DR. F. E. HACKETT, M.A.]

[Read April 26. Published October 11, 1920.]

Synopsis:—*Distillation of dilute solutions*; *electrolytic dissociation.*—An attempt is made to explain the deviations from the distribution law observed when dilute solutions of volatile fatty acids are distilled. The evidence indicates that it is probably due to electrolytic dissociation, since the deviation increases with the dilution, and is most marked with acids possessing a comparatively large dissociation constant. The possibility of the occurrence of molecular complexes in the solution or of hydration of the solute does not explain the experimental results. An expression has been deduced to represent electrolytic dissociation during distillation, and to correct the distillation constant. Applying the corrections for electrolytic dissociation, it is found that the distillation constants are practically independent of the concentration, provided that the solution is not highly concentrated.

The addition of salts.—It is found that the addition of salts to solutions of acetic and butyric acids increases the distillation constant in most cases. It seems probable that this cannot be explained by assuming a suppression of the ionisation of the acid, or an increase in the boiling-point of the solution.

In a previous publication the authors emphasized the fact that the distillation constants of the lower saturated fatty acids were not constant, but varied with the concentration.[1] An investigation was undertaken to determine the nature of this disturbing influence. Since the effect appears to be connected with the change in concentration, a method of distillation had to be chosen in which there was a considerable change in the concentration of the solution. The distillation at varying volume fulfils these conditions, and the experimental data was collected almost exclusively from distillations with a progressively diminishing volume. Some experiments were carried out using a progressively increasing volume of liquid in the flask, but the results were not so uniform as when the volume diminished.

The apparatus employed consisted of a round-bottomed flask of about 400 c.c. capacity. A steam-jacket surrounded the flask in the manner already described in a previous publication (*loc. cit.*). An electric hot-plate was used

[1] Sci. Proc. Roy. Dub. Soc., xv, 37, 513.

for heating. The distillate was collected in weighed cylinders, provided with stoppers, in approximately equal fractions of 10 grammes each. Throughout this investigation standardized barium hydroxide solution, approximately 0·1 N, was used in titrating the distillate, precautions being taken to eliminate the effect of carbon dioxide.

For the interpretation of the experimental results an expression was calculated from Nernst's law of distribution. From this law the following equation holds :—

$$\frac{dx}{dv} = \frac{k\sigma}{\rho} \cdot \frac{a - x}{V - v},$$

where x = acid in vol. v of distillate,

a = initial acid in vol. V in flask,

$a - x$ = acid in flask at any time in vol. $V - v$.

Integrating $$\frac{a - x}{a} = \left(\frac{V - v}{V}\right)^{\mu}$$

where $$\mu = \frac{k\sigma}{\rho},$$

from which it follows that $\log a - \log (a - x) = \mu [\log V - \log (V - v)]$.

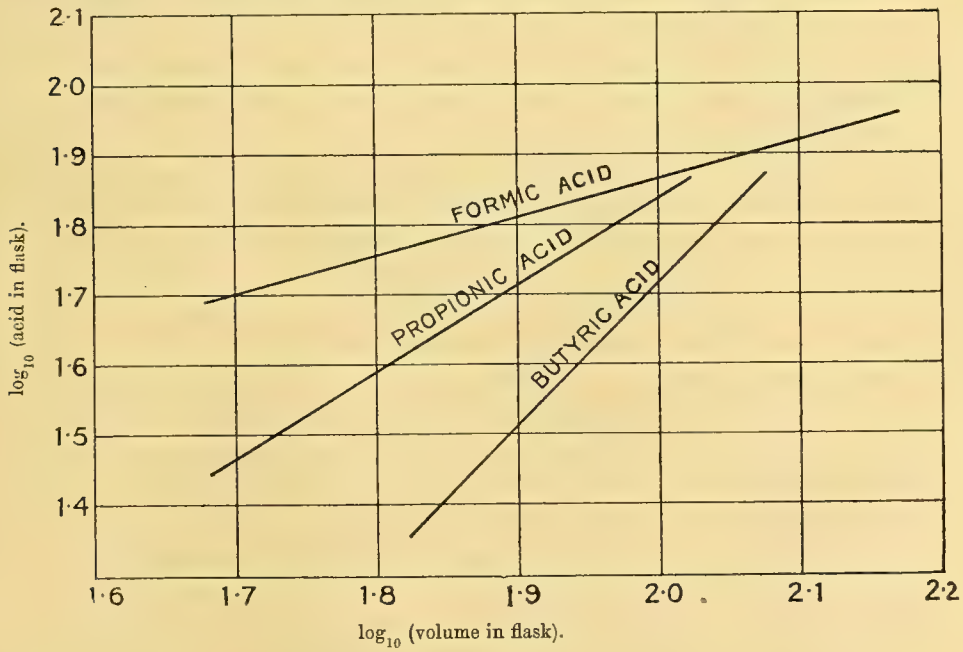

Fig. 1.

The values of log (acid in flask) have been plotted against the values of log (volume in flask), fig. 1. The line joining the experimentally derived

values approximates to a straightl-ine, but with formic acid there is a deviation (only apparent on a large-scale drawing).

This variation in the distillation constant may be due to several causes.

(*a*) Variation in experimental conditions, such as irregular rate of distillation, condensation in the still-head, &c.

(*b*) Impurities in the acids employed.

(*c*) Changes in the volumes of dilute solutions of the acids on further dilution.

(*d*) Deviation from the distribution law.

The variations due to irregular condensation are reduced to a minimum by surrounding the still-head with a steam-jacket, so that the temperature is maintained at 100°. If the still-head were below 100°, condensation would occur until the temperature had increased sufficiently for an equilibrium to exist between the liquid and the vapour. When the temperature of the still-head is above the boiling-point of the solvent in the flask, drops of the solution which may have been carried into the neck of the flask become completely volatilized, and in consequence an error is introduced. These effects will not occur if the temperature of the neck is kept at the boiling-point of the solvent used in the flask. Heating the flask by means of an electric hot-plate secures a regular rate of ebullition, and therefore the distillation will be regular if condensation is absent.

Care was taken in preparing the acids for this investigation to obtain them in as high a state of purity as possible. It is probable that the formic, acetic, propionic, *n*-butyric, and *n*-valeric acids used by the authors contained no more than traces of impurities.

The changes in volume on diluting the distillate, consisting of a dilute solution of a fatty acid, with a solution of different concentration, are probably negligible. A slight error, however, is introduced in assuming that the weight of the distillate is equal to the weight of water contained in it. Although the error is slight, it does not account for the alteration of the constants with dilution. The effect is more marked in the case of formic and acetic acids, where the error (due to assuming that the weight of distillate is equal to the weight of water contained in it) is less than in the case of the higher acids.

In deducing expressions for the interpretation of the experimental results it was assumed that there was no deviation from Nernst's law with change in concentration. This assumption is not strictly justifiable, since changes in molecular aggregation occur on diluting certain solutions.

It is well known that in the liquid state formic and acetic acids are associated, and also, to a less extent, the higher acids. It is probable that in aqueous solution the molecular complexes are broken down into single molecules, the dissociation increasing with the dilution.[1] If the dissociation has not proceeded to completion at the dilution employed, the experimental results will be further influenced by the breaking down of molecular complexes into simpler aggregates. It might, however, be expected that in very dilute solutions the dissociation would be complete, and, consequently, that the constants would reach a limiting value. The experimental evidence does not support this.

H. C. Jones[2] has suggested that in aqueous solution some part of the water is combined with the dissolved substance to form a hydrate. The amount of hydration increases with the dilution. This may also be a factor which influences the distillation constant.

In dilute aqueous solutions the lower fatty acids are partly dissociated into ions, and there will be a progressive alteration in the dissociation on increasing the dilution, if it be assumed that the ions take no part in the distillation. It is seen that ionisation has the effect of reducing the actual concentration of the undissociated acid. The values for the distillation constant, calculated on the assumption that the concentration of the acid in the solution is equal to that determined by titration, must be corrected therefore for the ionisation. The values calculated directly from the experimental results will become less with increasing dilution, if the ionisation of the acid is not taken into account.

The dissociation of a weak electrolyte in solution can be represented by the following equation:—

$$\frac{\alpha^2 c}{1 - \alpha} = k,$$

where $c = \frac{1}{v}$

(v = volume in litres containing 1 gram mol.),

α = dissociation,

or $\alpha^2 = k/c$, where α is small.

The equation

$$\frac{dx}{dv} = \mu \left[\frac{a - x}{V - v}\right]$$

[1] Cf. Murray, Amer. Chem. Journ., 1903, 30, 193.
[2] Amer. Chem. Journ., 1900, 23, 103.

must be corrected by the factor for dissociation

$$1 - \alpha = (1 - \sqrt{k/c})$$

or

$$\frac{dx}{dv} = \mu \frac{a - x}{V - v} - \mu \sqrt{k} \frac{\sqrt{a - x}}{\sqrt{V - v}}.$$

The equation becomes :—

$$\frac{\sqrt{a-x} - \frac{\mu\sqrt{k}}{\mu - 1} \cdot \sqrt{V - v}}{\sqrt{a} - \frac{\mu\sqrt{k}}{\mu - 1}\sqrt{V}} = \left[\frac{V - v}{V}\right]^{\frac{\mu}{2}}$$

since initial dissociation

$$\alpha_0 = \sqrt{k}\sqrt{\frac{V}{a}}$$

and

$$\alpha = \sqrt{k}\sqrt{\frac{V - v}{a - x}}.$$

Substituting these values

$$\frac{\sqrt{a-x}\left[1 - \frac{\mu}{\mu - 1}\alpha\right]}{\sqrt{a}\left[1 - \frac{\mu}{\mu - 1}\alpha_0\right]} = \left[\frac{V - v}{V}\right]^{\frac{\mu}{2}}$$

or by obvious approximations

$$\sqrt{a-x} = \left[\frac{V - v}{V}\right]^{\frac{\mu}{2}} \cdot \sqrt{a}\left[\frac{1 - \frac{\mu}{\mu - 1}\alpha_0}{1 - \frac{\mu}{\mu - 1}\alpha}\right]$$

$$= \left[\frac{V - v}{V}\right]^{\frac{\mu}{2}} \cdot \sqrt{a}\left[1 - \frac{\mu}{\mu - 1}(\alpha_0 - \alpha)\right]$$

$$= \left(\frac{V - v}{V}\right)^{\frac{\mu}{2}} \cdot \sqrt{a}\left[1 - \frac{\mu}{\mu - 1}\alpha_0\left[1 - \left(\frac{V}{V - v}\right)^{\frac{\mu - 1}{2}}\right]\right]$$

$$\text{or } \log(a - x) = \mu \log(V - v) - \mu \log V + \log a + 2\log\left[1 - \frac{\mu}{\mu - 1} \cdot \alpha_0\left(1 - \frac{V}{V - v}\right)^{\frac{\mu - 1}{2}}\right]$$

$$\frac{\log a - \log(a - x)}{\log V - \log(V - v)} = \mu - \frac{2\log\left[1 - \frac{\mu}{\mu - 1}\alpha_0\left[1 - \left(\frac{V}{V - v}\right)^{\frac{\mu - 1}{2}}\right]\right]}{\log V - \log(V - v)}.$$

The left-hand side expression is the μ calculated from the observed results = μ_a.

$$\mu_a = \mu - \frac{\frac{2\mu}{1-\mu}\, a_0 \left[1 - \left(\frac{V-v}{V}\right)^{\frac{1-\mu}{2}}\right]}{\log V - \log (V-v)}.$$

When the volume distilled is small compared with the total volume,

$$\mu_a = \mu - \mu a_0 \text{ approximately} = \mu\,(1 - \sqrt{k/C_0}\,),$$

where C_0 is the concentration initially in the flask for the range over which μ_a has been calculated.[1]

In Table I the experimentally derived values for μ_a are given, and also the values of the constant after correcting for the ionisation of the acid.

Table I.

Formic Acid.

Wt. of Sol. in flask. (grams.)	Acid in flask.*	μ_a observed.	μ corrected for ionisation.
150·00	89·3	0·437	—
139·23	86·44	0·456	0·484
127·41	83·01	0·465	0·493
116·70	79·70	0·464	0·492
106·13	76·26	0·458	0·485
95·36	72·64	0·466	0·492
84·51	68·64	0·473	0·498
73·51	64·28	0·472	0·496
62·26	59·42	0·475	0·499
51·16	54·12	0·478	0·499

* No. of c.c. 0·1 N.$Ba(OH)_2$ to neutralize.

The values for the other acids are also tabulated (Table II).

---

[1] In the calculations the following values for the dissociation constant k have been taken :-

Formic acid	$2{\cdot}1 \times 10^{-4}$
Acetic acid	$1{\cdot}8 \times 10^{-5}$
Propionic acid	$1{\cdot}3 \times 10^{-5}$
n-Butyric acid	$1{\cdot}5 \times 10^{-5}$

With reference to the calculation of μ_a, this has been done by substituting the appropriate values of a, x, V, and v in the formula :—

$$\frac{\log a - \log (a-x)}{\log V - \log (V-v)}.$$

TABLE II.

	Dilution. (Litres containing 1 gram mol.)	μ_a observed.	μ corrected for ionisation.
Acetic acid, . .	22·5	0·687	0·707
„ „ . .	11·0	0·698	0·709
„ „ . .	3·5	0·703	0·708
Propionic acid, .	13·0	1·22	1·24
n-Butyric acid, .	13·0	1·94	1·97

Richmond[1] has investigated the change of the distillation constant of formic acid with alterations in concentration of the solution. The following table records his values, and also our values after correction has been made for ionisation :—

TABLE III.

Dilution. (Litres containing 1 gram mol.)	μ_a observed.	μ corrected for ionisation.
77·0	0·402	0·461
58·9	0·4065	0·457
33·3	0·416	0·454
24·4	0·419	0·449
20·0	0·4205	0·449
16·7	0·4225	0·449
12·8	0·4230	0·446
9·27	0·427	0·447
8·0	0·432	0·450
6·25	0·437	0·453
4·32	0·437	0·450
3·71	0·441	0·454
2·92	0·440	0·451
2·44	0·443	0·453
1·96	0·443	0·452
1·30	0·442	0·449

[1] Analyst, 1908, 33, 305.

In the following table the recorded values for acetic acid (*ibid.*) are given, and also the values after correction for ionisation .—

Table IV.

Dilution. (Litres containing 1 gram mol.)	μ_a observed.	μ corrected for ionisation.
68·0	0·680	0·705
35·4	0·683	0·701
17·5	0·685	0·698
6·90	0·692	0·700
3·54	0·697	0·703

It can be seen from Tables I–IV that by applying a correction for the ionisation of the acid in the solution a constant is obtained. The value of the constant thus obtained is practically independent of the concentration. Thus the principal variation in the distillation constants of the volatile fatty acids with dilution can be accounted for by taking the ionisation into consideration. The values in fig. 2 are the comparative results from several experiments, but the figures are not absolute.

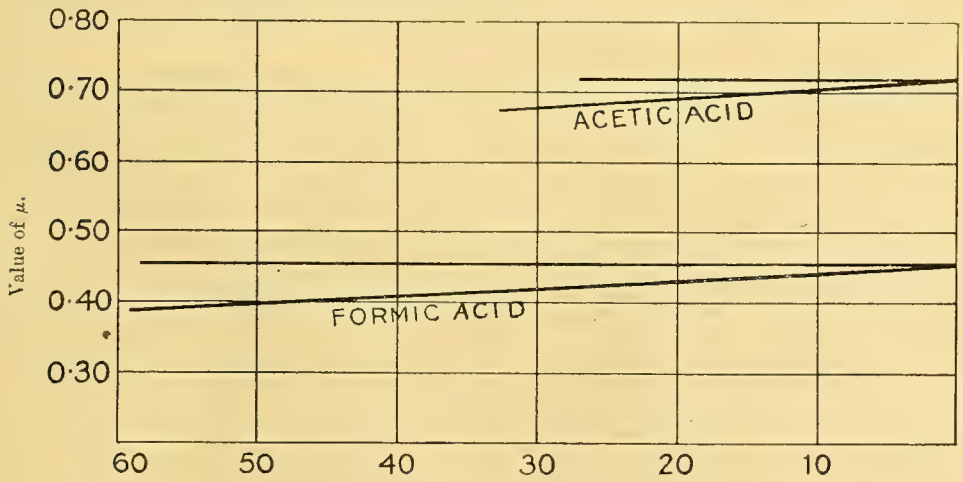

Fig. 2.

The Addition of Certain Acids and Salts.

It has been shown by Stein[1] that the addition of sulphuric acid to an aqueous solution of acetic acid increases the distillation constant.

[1] J. pr. Chem., 1913, **88**, 83.

In the following table the qualitative effect of the addition of acids is shown, the distillation being carried out at constant volume.

TABLE V.

Titration.

Weight of successive fractions in grammes.	Amount in c.c. of 0·1 N. $Ba(OH)_2$ to neutralize each fraction. 1.	2.	3.	4.
10	4·07	6·04	5·77	5·84
10	3·86	6·12	5·49	5·60
10	3·62	5·39	4·82	5·50
10	3·54	4·79	4·71	5·34
10	3·39	4·59	4·49	4·84

The solutions had the following compositions:—

1. 100 c.c. of dilute acetic acid + 50 c.c. water.
2. „ „ „ + 50 c.c. of phosphoric acid.
3. „ „ „ + 50 c.c. of sulphuric acid
4. „ „ „ + 50 c.c. of oxalic acid solution.

These results are not comparable, but they show that acids other than sulphuric acid considerably influence the distillation constant.

The addition of a neutral salt to a solution of a weak acid, such as acetic, will have a small influence on the degree of dissociation. If a salt of the acid is added, an ion is introduced into the solution which is common to both electrolytes.[1] A considerable suppression of the ionisation of the acid will occur if the salt added is ionised to any great extent. Sodium acetate when added to acetic acid considerably reduces the dissociation of the acetic acid. It might be expected that the distillation constant of acetic acid in presence of sodium acetate would be approximate to that for the undissociated acid.

[1] In a recent paper, published since the present work had been completed, M'Bain and Kam (Trans. Chem. Soc., 1919, 115, 1332) have recorded an investigation into the effect of the addition of certain salts to acetic acid. They determined the ratio of acetic acid in the vapour to that in the liquid phases for the pure aqueous solutions, and solutions containing dissolved salts. They suppose that the addition of a salt enhances the chemical potential of the acid, and as a consequence there is an increase in the vapour tension of the acid. They also found that there was a considerable variation in the effect when different salts were employed. [Cf. Reilly and Hickinbottom, Brit. Assoc. Ann. Report, 1919, p. 170.]

Experiments were carried out, adding 50 c.c. of a normal solution of sodium acetate to 100 c.c. of acetic acid, the determination of the distillation constant being made in the usual manner. To compensate for the increased boiling-point of the solution, the constant was determined in presence of other salts of the same molecular concentration.

The results are given in Table VI, and the percentage increase is given. The results cannot be explained simply. It is noteworthy that sodium acetate causes only a slight increase in the constant compared with other salts, while the presence of copper sulphate actually reduces the distillation constant. Further, the retarding influence of copper sulphate is shown when a dilute butyric acid solution (containing copper sulphate) is distilled. No other salt among those examined appears to have a similar effect at the dilution employed, although several other substances were studied. It is possible that in some cases, *i.e.*, copper sulphate, in addition to a physical alteration in the solution, there may also be some chemical change.

Table VI.

Substance added.	μ observed.	per cent. variation.
None, . . .	0·690	—
Sodium acetate, . . .	0·726	+ 5·2
Potassium chloride, . .	0·780	+ 13·0
Potassium iodide, . .	0·762	+ 10·4
Sodium chloride, . .	0·766	+ 11·0
Potassium sulphate, . .	0·761	+ 10·3
Sodium nitrate, . . .	0·763	+ 10·6
Magnesium sulphate, . .	0·781	+ 13.2
Zinc sulphate, . . .	0·754	+ 9·3
Strontium chloride, . .	0·793	+ 14·9
Copper sulphate, . .	0·655	− 5·1

It appears that the alteration in the ionisation of the acid cannot account for the results, for sodium acetate has less effect than any of the other salts, except copper sulphate. Similarly an increase in the boiling-point of the solution does not explain the variation in the constants.

[Summary.

SUMMARY.

The deviations in the distillation constants of the lower fatty acids, especially in the case of formic and acetic acids, may be explained satisfactorily by taking into account the electrolytic dissociation of the acid.

By applying a correction for the electrolytic dissociation, the distillation constant is independent of the dilution.

The addition of certain salts and acids increases the distillation constant, but the amount of increase appears to depend on the nature of the salt added. The addition of a solution of copper sulphate, containing 1 gram molecule per litre, to a dilute acetic acid solution causes a diminution in the distillation constant.

The authors have much pleasure in thanking Dr. F. E. Hackett for the assistance which he has given them during the progress of the work.

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BY

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AND

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Smithsonian Institution
MAR 5 1921
National Museum

[COMMUNICATED BY DR. F. E. HACKETT, M.A.]

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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MAR 5 1921

XII.

NOTES ON SOME APPLICATIONS OF THE METHOD OF DISTILLATION IN STEAM.

By JOSEPH REILLY, M.A., D.Sc., F.R.C.Sc.I.,

AND

WILFRED J. HICKINBOTTOM, B.Sc.

[COMMUNICATED BY DR. F. E. HACKETT, M.A.]

[Read April 26. Published October 11, 1920.]

Synopsis.—*Distillation of dilute solutions*; *Applications.* The limitations and possibilities of the distillation method for determining molecular structure are discussed. A consideration of the distillation constants of a number of compounds shows that, although the molecular structure may be inferred in certain cases, this method cannot be applied generally without the support of further evidence.

Determination of changes in state of molecular aggregation. The distillation constant is deduced from Nernst's law of distribution; consequently any alteration in the state of molecular aggregation during distillation will alter the distillation constant. A scheme has been proposed by which it is possible to follow any change in the solute occurring in solutions the concentrations of which differ widely.

A method has also been devised to differentiate butter-fat from other fats containing a comparatively high proportion of volatile acids. It is based on the presence of butyric acid in butter-fat, while this acid does not occur in appreciable amounts in other fats of the types examined.

The distillation constants of the lower fatty acids containing a normal chain rise in an approximately regular manner with increasing molecular weight. With acids in which a branched chain occurs the distillation constants are higher than those containing a normal chain. They correspond approximately with the distillation constants of the next higher member in the series of normal compounds.[1] These facts suggest that the regularity may be general. The determinations of the distillation constants of the lower aliphatic alcohols showed that in this series there was also a parallel between the distillation constant and the molecular weight. Furthermore, the distillation constants of isomers were higher if the chain of carbon atoms was not a normal one.

It appears, therefore, in the homologous series of saturated aliphatic alcohols and acids that the distillation constant of the substance may be deduced if the molecular configuration of the acid and its molecular weight are known.

[1] Reilly and Hickinbottom, Proc. Royal Dub. Soc., xv, 37, 513.

Table I gives the constants calculated from values recorded in the literature[1] for acids other than the volatile fatty acids. Table II gives the data for the latter acids.

TABLE I.

	μ		μ
Benzoic, . .	0·22	*p*-Toluic, . .	0·33
o-Toluic, . .	0·51	*o*-Hydroxy benzoic,	0·09
m-Toluic, . .	0·40	*p*-Hydroxy benzoic,	very small

The acids, glycollic, monochloracetic, oxalic, malonic, mandelic, and phenylacetic, have small distillation constants. "Nitroglycerine" is also distillable in steam, and its distillation constants are now being determined.

TABLE II.

	$\left[\frac{1}{v}\log\frac{a}{a-x}\right]$*	$[x]$†	Boiling-point [760 mm.] °C.
Formic acid, .	0·00128	3·61	100·6
Acetic acid, .	0·00215	3·61	118
Propionic acid, .	0·0036	1·79	140
n-Butyric acid, .	0·0055	1·57	163
iso-Butyric acid, .	0·0073	1·44	155

* The initial volume of solution in the flask, 150 c.c.

† Ramsay Shields' association factor.

The authors[2] have also investigated the rate of steam distillation of the lower alcohols. The values obtained for $\left[\frac{1}{v}\log\frac{a}{a-x}\right]$ are given in the following table, and the comparative values for x are also recorded :—

TABLE III.

	$\left[\frac{1}{v}\log\frac{a}{a-x}\right]$	$[x]$	Boiling-point [760 mm.] °C.
Methyl alcohol, .	0·015	3·44	66
Ethyl alcohol, .	0·024	2·75	78·3
n-Propyl alcohol, .	—	2·27	97·4
n-Butyl alcohol, .	0·040	1·95	117
iso-Butyl alcohol, .	0·066	—	108
sec-Butyl alcohol, .	0·066	—	99·8
iso-Amyl alcohol .	0·072	—	131

[1] Cf. Stein, J. Pr. Chem., 1913, 88, 83.

[2] Unpublished work (J. R. and W. J. H.) which will be submitted in detail to the Royal Dublin Society later in 1920.

Hausbrand[1] states that the composition of vapours (from liquids which mix with water) depends, "according to certain laws, upon the composition of the boiling mixture of liquids, but, unfortunately, is not accurately known for most mixtures of liquids, although this property is utilized on the largest scale in the industries for the distillation of such liquids." Even in the case of a liquid which does not mix with water, part of the liquid may be mechanically "taken away" with the steam, and for some substances the process of "blowing over" with saturated steam has wide industrial applications. Hausbrand gives the following approximate data for the amount of steam required to "carry over" 100 kilograms of various substances:—

Toluene requires . .	13–15 kilos of steam
Benzene „ . .	25–28 „ „ „
Fatty Acids require .	100 „ „ „
Tar requires . .	150 „ „ „
Glycerine requires . .	250 „ „ „
Nitrobenzene „ . .	250–300 „ „ „
Nitrotoluene „ . .	400–450 „ „ „

(1 kilo of steam at atmospheric pressure represents 637 calories.)

No differentiation is made between the cases in which mixtures of constant boiling-point, or of mechanical carrying over of the liquid in the current of steam, occur. Many other substances are purified by distillation in steam, such as various "intermediates" (e.g., aniline, orthonitrophenol, chloropicrin, etc.), petroleum products, essential oils, various esters, lactic acid, etc.

It should be noted that even among compounds closely related, the vapour pressures at 100° may differ widely, and no *a priori* reasoning, without actual experiment, can decide which compound will distil the more readily in steam. The results recorded above indicate in a broad manner the effect on the distillation constant of introducing various groups into the molecule. A phenyl group reduces the distillation constant, while an hydroxyl group replacing a carboxyl group causes an increase. When, however, carboxyl and hydroxyl groups are present in the molecule, the distillation constant is generally less than that of a compound containing only one of these radicles. The distillation constant is affected in a striking manner by constitutive differences in isomeric substances, and, as far as can be judged from the limited number of observations available, the influence of constitution on the distillation constant appears to be general.

The constants of acids and alcohols containing a branched chain are higher

[1] Evaporating, Condensing, and Cooling Apparatus, 2nd ed., pp. 19–20.

than those of isomeric substances in which the carbon chain is a normal one. In the aromatic series the position of the substituent group in the benzene ring has an influence on the distillation constant. Both in the case of the cresols and the toluic acids the *ortho* compound has a greater distillation constant than either the *meta* or the *para* derivatives.

It is noteworthy that the distribution of *o*-, *m*-, and *p*-toluic acids between liquid and vapour phase in dilute solution bears the same relationship to each other and to the constant for benzoic acid as the constants of *o*-, *m*-, and *p*-cresol and phenol. The distillation constants of *n*- and *iso*-butyric acids show a similar relation to those of *n*- and *iso*-butyl alcohols. The influence of constitution on the distillation constant is shown by *o*- and *p*-hydroxy-benzoic acids, and by *o*- and *p*- nitro-phenols. The results in the case of substances only sparingly soluble in water may be explained by a difference in the vapour-pressure of the substances at the boiling-point of the solution.

In the case of phenols and the lower fatty acids and alcohols the distillation constant appears to bear no relationship to the vapour-pressure. Pure methyl alcohol at 100° exerts a greater vapour-pressure than any of the other homologous alcohols, yet in dilute aqueous solution there is a smaller distribution coefficient between liquid and vapour phases than is the case with ethyl, butyl, or amyl alcohols. It seems to indicate other factors which influence the distillation of aqueous solutions. The molecular weights of the substance distilled have an influence in comparative distillations of members of a series of compounds. In Tables II and III a comparison is made between the Ramsay-Shields' association factor x, the distillation constant, and the boiling-point. It is seen that as the association factor decreases the distillation constant increases.

The association factor refers to the pure liquids; consequently no direct comparison can be made between the molecular state of the pure liquid and its aqueous solution. It shows, however, that for the lower members, as the homologous series is ascended, a gradual modification occurs in the attractions or forces exerted between the molecules. The inter-molecular forces are also modified by solution owing to the force exerted by molecules of the solvent on those of the solute. For miscible liquids or soluble substances, the greater the difference between the mean attractions of the molecules of the solute for each other and the solute for the solvent, the more abnormal will be the behaviour of the solution on distillation.[1] With the lower fatty acids and alcohols a gradual diminution with increasing molecular weight occurs in the attraction between molecules of

[1] Cf. Berthelot, Compt. Rend., 1898, 126, 1703.

the solvent and solute, using water as solvent. When such disturbing influences have been eliminated, it might be expected that the distillation constants and the vapour-pressures should be in proportion. The distillation constants of the fatty acids and the alcohols should reach a maximum, and then decrease with increasing molecular weight. Such has been found to occur in the fatty acid series. Distillations of aqueous suspensions of lauric and myristic acids were carried out. These acids are practically insoluble in water, consequently the effect of the solvent is eliminated. It was found that the distillate from the lauric acid suspension was richer in acid than that from the myristic acid-water mixture.

The results obtained by distilling dilute solutions of the volatile fatty acids show that with the method it is possible to detect alterations in the state of molecular aggregation. The success of the method depends on :—

(*a*) Constant temperature of distillation, and freedom from variations caused by irregular heating or condensation.

(*b*) Convenient and accurate method of estimating the solute.

(*c*) Choice of a suitable solvent.

To maintain a constant temperature, the solution must necessarily be of such a dilution that changes in concentration do not affect the boiling-point appreciably. This can be achieved by allowing only a small change in concentration, or by employing very dilute solution, such that the boiling-point approximates to that of the solvent. It is, however, possible to correct for change of temperature, and an apparatus has been devised so that distillation can be carried out over a considerable range of concentration and temperature of ebullition. It is intended to describe this at some future date.

The solute need not necessarily be a volatile fatty acid, and the choice of a solute is restricted only by the solubility in the solvent and its volatility. It is, however, essential that an accurate method should be available for the estimation of the solute. By using the same solute in a series of different solvents, and employing a considerable range of concentration, evidence may be obtained concerning the actual state of substances in solution. This applies more particularly to concentrated solutions, which cannot be conveniently investigated by methods involving the principles of osmotic pressure.

The method of distillation of dilute aqueous solutions has been applied chiefly for the detection and estimation of mixtures of fatty acids. It is from this point of view that most of the investigations have been carried out, and the conditions determined for obtaining accurate results.[1] It follows

[1] Upson, Plum, and Schott. J. Amer. Chem. Soc., 1917, 39, 731 ; Lamb, *ibid.*, 1917, 39, 746. Gillespie and Walters, *ibid.*, 1917, 39, 2027 ; Richmond, Analyst, 1919, 44, 255.

from the variation of distillation constant with dilution that this factor should not be neglected. Similarly, the presence of non-volatile impurities in the solution may have a considerable influence on the result.

A comparison of butter-fat with other edible fats and oils shows that while most of the fats are glycerides of acids of higher molecular weight than caproic, butter contains an appreciable amount of butyric acid. It might be expected that the acids from butter-fat could be distinguished from those of the other fats by their distillation constant. Preliminary experiments confirmed this view, and a method has been worked out for determining the distillation constants of the volatile acids in fats.

The principles underlying the distillation of dilute solutions have been applied in certain industrial processes. In the purification of alcohols, use is made of the fact that in dilute solutions the higher alcohols are removed more rapidly than the lower ones. This is the principle involved in the Guillaume stills for alcohol distillation. A dilute solution of the raw spirit is distilled when the fusel-oils are removed in the first portion of the distillate, while an aqueous solution of ethyl alcohol remains in the still.

The addition of salts, in increasing the distillation constant of acetic acid, is the basis of one of the methods which have been employed for obtaining concentrated acetic acid from dilute aqueous solutions. It is uneconomical to do this by simple fractionation of the vinegar. The method as used industrially consists in distilling the dilute solution in presence of a salt, so that the distillate is richer in acetic acid than the original solution.

The Distillation of Aqueous Solutions of Lauric and Myristic Acids.

In order to determine if the increase in the distillation constant was general as the homologous series ascended, the constants of lauric and myristic acids have been determined.

These acids occupy in the fatty acid series a position removed from acetic and butyric acids. They are almost completely insoluble in water; consequently it may be assumed that heat of solution and volume changes on mixing are eliminated.

A known weight of the pure acid was added to a known volume of distilled water. The resulting mixture was then distilled in a round-bottomed flask, surrounded by a steam-jacket, in the same way as described for previous experiments. It was found that on conducting preliminary experiments, a considerable amount of the acid solidified in the condenser, and vitiated the results to some extent.

The defect was remedied by using a special condenser arranged so that it could be kept at a temperature above the melting-point of the acid used.

This could be arranged either by making the jacket of the condenser part of a warm-water circulation system, or by supplying cold water to the condenser in a very slow stream, so that the acid does not solidify.

The former method is the one more easily regulated, and it is convenient for a number of determinations. Diagram shows the apparatus as finally set up, and as used for the distillation of aqueous suspension of lauric and myristic acids. [Fig. 1.]

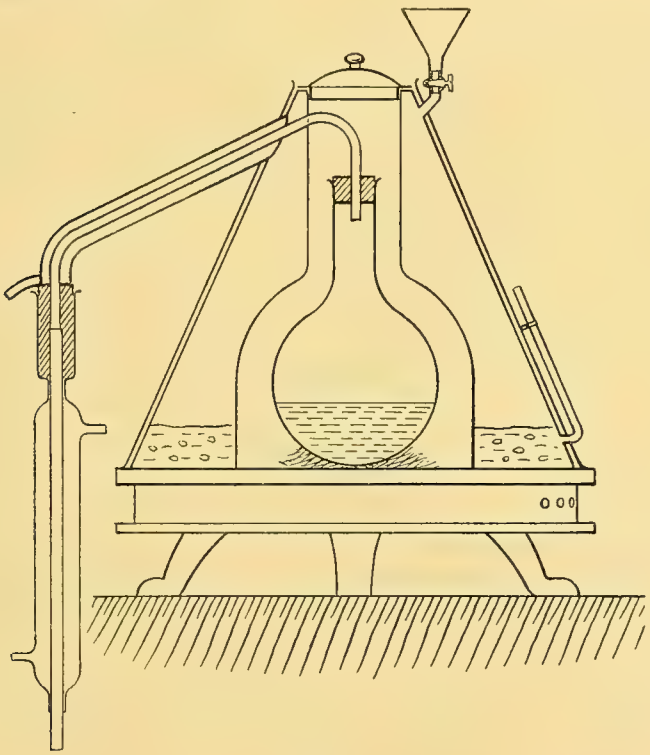

Fig. 1.

The mixture of acid and water was collected in a series of weighed cylinders. The distillate was washed out by means of neutral alcohol, and the washings were repeated until all the acid had been dissolved. It was then titrated with standard barium hydroxide solution, using phenolphthalein as an indicator. It was considered better in the case of these acids to obtain a constant depending on the ratio of acid to water in the distillate, and to neglect the acid originally present in the flask.

Supposing the system to be a mixture of immiscible and unlike liquids, the amount in the flask should not have any effect. Using a considerable excess of acid this holds approximately, but it is found that

when small amounts of acid are used errors are introduced, probably owing to particles of the liquid adhering to the walls of the flask.

The experimental results are given in Table IV, and constant C in the formula has been determined:

$$C = \frac{W_a \times M_w}{W_w \times M_a'}$$

where W_a and W_w are weights of acid and water, M_a and M_w are molecular weights of acid and water, C = ratio of vapour tensions at 100°.

The constant C, when immiscible and unlike components are used, is ratio of the vapour-tensions of the two substances.

The constant has therefore been used to calculate the vapour tension of lauric and myristic acids. The temperature of the liquid is taken as 100°—the boiling-point of distilled water—because the amount of the acids present and their insolubility in water render it improbable that they will affect the temperature of boiling to any appreciable extent.

On account of the relatively small amount of acid present, the vapour pressure is taken as atmospheric.

The calculated vapour tensions are lower for myristic than for lauric acid.

TABLE IV.

Lauric Acid.

Composition of distillate.		C	Vapour tension (calculated).
Water.	Acid.		
30·11	0·0256	$7{\cdot}6 \times 10^{-5}$	0·058 mm.

Myristic Acid.

60·45	0·0327	$4{\cdot}3 \times 10^{-5}$	0·033 mm.

These results are the mean of several determinations.

The Distillation of Aqueous Solutions of Phenols.

For the estimation of phenols in aqueous solution the method due to Messinger and Vortmann[1] was employed.

The method consists in adding a known amount of standard iodine solution to the phenol at a suitable concentration in presence of approximately three molecular proportions of sodium hydroxide, and heated to 60°. The iodine is added until the liquid assumes a yellow colour, and a yellowish curdy precipitate separates on shaking. The solution is cooled, diluted to a

[1] Ber., 1889, 22, 2313. Cf. Bergault. J. Pharm. Chem., 1908, 28, 45.

known volume, and a measured portion of the diluted solution is withdrawn, filtered, and titrated with standard sodium thiosulphate, after rendering it faintly acid. From a knowledge of the amount of iodine used originally, and the volume of thiosulphate required for the final titration, the amount of phenol present in the solution can be obtained. It was found advisable during these experiments to determine the amount of iodine required for a known weight of each phenol before proceeding with the actual determinations.

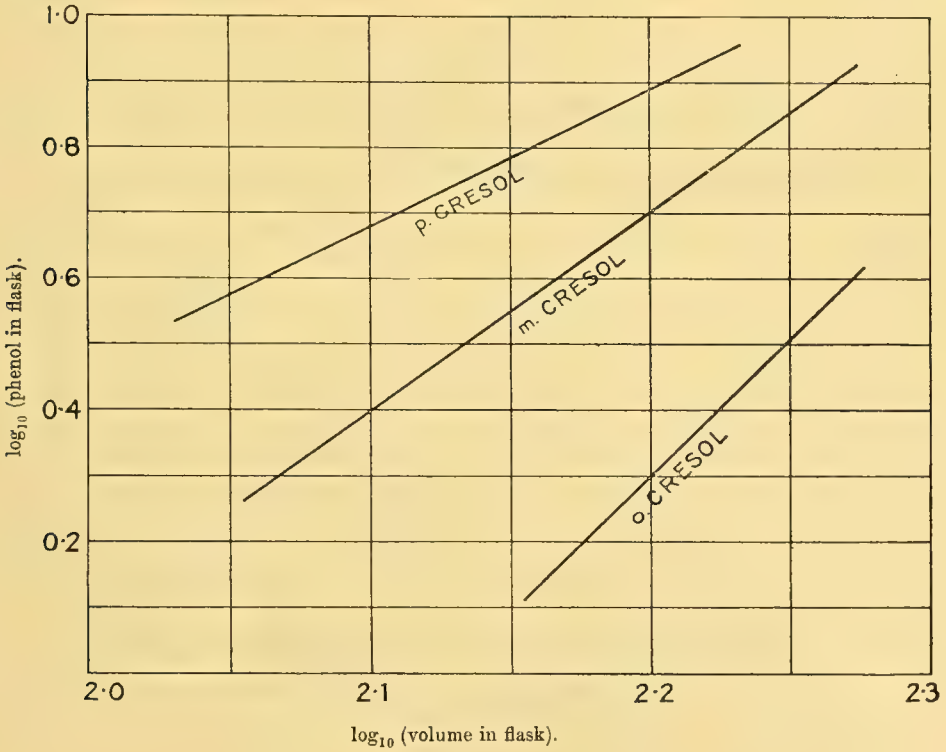

Fig 2.

The phenol employed was white, and had been purified before use. *o*-Cresol was obtained from pure *o*-toluidine by means of nitrous acid, and it was fractionally distilled before use. *p*-Cresol was bought as pure, and was not further purified. It had a melting-point of 36·3° (uncorrected), and was white in colour.

A solution of the phenolic body was prepared, containing a known weight of the substance. The amount of iodine required to precipitate the phenol in an aliquot part was determined, and the mean of all the determinations taken.

200 c.c. of the phenolic solution were distilled in a round-bottomed flask, heated on an electric hot plate, and surrounded by a steam-jacket, the usual precautions being taken to ensure regular ebullition, and to prevent access of cooling draughts. The distillate was collected in weighed stoppered cylinders, approximately 10 grams of distillate being collected in each fraction. The exact weight was obtained in each case by weighing the full cylinders. For the estimation of the phenolic substances in each fraction the distillate was diluted to a suitable concentration, and the estimation carried out as described above.

The values $\log_{10}$ (cresol left in flask) were plotted against $\log_{10}$ (volume left in flask). The points obtained fell along a straight line. Then the value of μ, the distillation constant, is given by the slope of the line joining the points determined experimentally. See fig. 2.

The following distillation constants were determined :—

TABLE V.

	μ
Phenol, .	1·7
o-Cresol, .	4·2
m-Cresol, .	3·15
p-Cresol, .	2·2

Comparative Distillations in Steam of Acids from Butter and other Products.

As well as using the method of steam distillation for the analysis and detection of mixtures of lower fatty acids, it may be applied to detect the presence of acids of comparatively low molecular weight in the presence of higher fatty acids.

Butter differs from most other fats in containing a relatively high percentage of butyric acid. The distillation constant of the volatile fatty acids from butter will, therefore, show a lower distillation constant than those from other fats. On this fact a process has been worked out by which butter-fat may be distinguished from other fats.

The Reichert-Meissl determination was carried out in the usual way, collecting 110 c.c. of distillation. 100 c.c. of the filtered distillate were titrated with a standard barium hydroxide solution to determine the concentration of acid in the distillate. The barium was precipitated by the addition of the calculated amount of sulphuric acid, and the solution made up to 200 c c. It was distilled in an ordinary round-bottomed flask, using a steam-jacket, and the distillate collected in 10-gram fractions, and titrated. The percentage of acid distilling in each fraction was calculated on the acid present in 100 c.c. of the original Reichert-Meissl distillate.

The results obtained with typical fats of high Reichert-Meissl value are given in Table VI. [See also Fig. 3.]

It can be seen that the values are sufficiently wide apart to differentiate between butter-fat and any of the fats employed in this investigation.

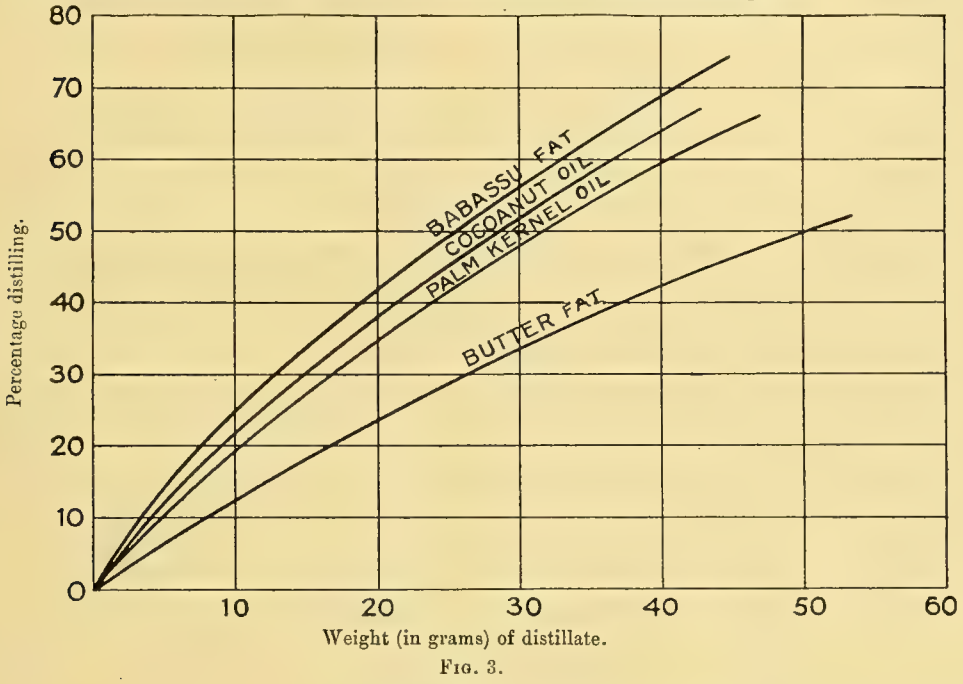

Fig. 3.

Table VI.

Wt. of distillate in grams.	Percentage Acid Distilling in each Fraction. Butter Fat.	Palm Kernel Oil.	Babassu Fat.	Cocoa Nut Oil.
10	12·5	20	25	22
20	23·0	35	42	38
30	35·5	49	57	53
40	42·5	60	70	65
50	50·0	68	80	75

The values for butter are the means of determinations on samples from three different sources.

The babassu fat[1] was about fifteen months old, and gave the following values:—

Melting-point,	25·5
Iodine value (Wijs),	15·5
Saponification value,	248
Acid value,	0·17
Reichert-Meissl,	5·8

[1] We are indebted to Mr. G. van B. Gilmour for this sample of babassu fat.

Distillation by Blickfield's process gave the following figures:—

Total volatile acids, ...	16·0 per cent.
Insoluble silver salts, ...	13·6 per cent.
Soluble silver salts, ...	2·4 per cent.
Melting-point of insoluble volatile acids, .	19·0°

SUMMARY.

The distillation constants of the fatty acids, alcohols, and phenols, soluble in water, bear a relation to the molecular structure of the substance.

The distillation of solutions containing a volatile solute can be applied to detect changes in the state of molecular aggregation.

The analysis of solutions of fatty acids by distillation may be extended to differentiate butter-fat from other fats containing a relatively high proportion of acids volatile in steam.

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THE DETERMINATION OF THE RATE OF SOLUTION OF ATMOSPHERIC NITROGEN AND OXYGEN BY WATER.

BY

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AND

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Smithsonian Institution MAR 5 1921 National Museum

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XIII.

THE DETERMINATION OF THE RATE OF SOLUTION OF ATMOSPHERIC NITROGEN AND OXYGEN BY WATER.

By W. E. ADENEY, D.Sc., A.R.C.Sc.I., F.I.C.,
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[Read April 27. Published September 17, 1920.]

Part III.—*The Rate of Solution of Air by Quiescent Waters under Laboratory Conditions.*

In previously published parts of this communication the rate of solution of gases by water, when thin films of the water are exposed to the gas or gases, and kept uniformly and rapidly mixed with the unexposed portions of it, has been dealt with, and shown to take place in accordance with a simple law.

With a view to deriving, if possible, a formula for the rate of solution of air by quiescent bodies of water, the results thus obtained have been applied to the elucidation of a number of experiments which had been previously made with small volumes of still water, and the results are given in this communication.

When the process of solution of air by water is considered, it is evident that it may take place in one of three ways—(1) Solution at the surface exposed to the air with thorough and rapid mixing with the unexposed portions; (2) solution at the surface with no mixing; (3) solution at the surface with slow or imperfect mixing.

The conditions stated under section (1) are practically those obtaining in the experiments already described, and hence under these conditions the formula already deduced would apply. However, these conditions do not ordinarily occur.

The conditions stated under section (2) are those which are commonly assumed to obtain, although there seems to be very little justification

for such an assumption in practice. Obviously if there be no mixing of the water, the only process by which the air can penetrate into the mass of the water is by diffusion of the dissolved gas molecules; hence the ordinary law for the diffusion of solutes would hold under these conditions. But there is no experimental evidence to show that such conditions ever occur under natural conditions; and it is doubtful if they have ever been produced artificially even in the laboratory. On the other hand, there is evidence to show that it is not possible to expose a mass of water to the air and still keep the exposed and unexposed portions of the water unmixed. Thus, when Huefner was determining the velocity of diffusion of dissolved gases in water, he found it necessary to expose the columns of water to the gas at the lower surface through the medium of a porous plate of hydrophane, in order to avoid the mixing that he found to occur when the upper surface of the columns of water was exposed to the gas. A considerable number of experiments made by one of the authors also points to the fact that the dissolved gases do not accumulate in the upper layers of a column of water exposed to the air, as they would tend to do if there were no mixing. Hence calculations based on the law of diffusion cannot be of any practical value.

The third set of conditions postulated, namely, solution at the surface with slow mixing, seems to be that which would occur most frequently in practice. Under these conditions the rate of solution will be dependent on the rate of mixing.

The formula applicable in this case might be expected to be of the same form as that already derived from the experiments with thin films, where the mixing was extremely rapid, but the constants will alter according to the rate of mixing. It will be shown that the results of the experiments quoted here can be approximately represented by an equation of the required form, and that the constants vary with (1) the humidity of the air in contact with the water, and (2) the salinity of the water.

The method of experimenting consisted in filling a number of tubes of about 30 cms. length and 4 cms. diameter with de-aerated tap-water, and inserting rubber-stoppers in such a way as to exclude all trace of air. The tubes were then placed in a thermostat until the water in them was at the same temperature as that of the thermostat. The corks were then removed, 50 cc. water withdrawn, and the water remaining in the tubes exposed to the air for periods of different length, and the air-content determined at the end of the exposure. The initial air-content of the de-aerated water having been previously determined, the data for calculating the rate of solution was then available.

The results of the experiments are given in Tables I and II.

TABLE I.

Experiments with columns of tap-water. Temperature, 15° C.

Area exposed.	Vol. of water.	Time of exposure.	Amount of air absorbed.	Degree of aeration in per cent. of saturation.	Value of '*b*' const.
		hours	0	13·8	
12·56	260	23·5	31·6	45·4	·019
12·56	260	48	55·3	69·1	·021
12·88	260	70	63·4	77·1	·019
12·88	260	93	71·6	83·6	·018
12·56	251	120	75·8	89·1	·018
12·56	260	141·5	79·7	92·1	·017
Mean 12·62	258				

TABLE II.

Experiments with columns of sea-water. Temperature, 15° C.

			0	13·7	
12·56	268	21·5	28·8	42·5	0·019
12·25	255	24·0	41·3	58·3	·029
12·88	270	24	42·2	56·1	·028
12·88	270	44	60·8	77·0	·029
12·88	270	72	70·4	86·5	·025
12·25	251	96	74·6	90·0	·022
12·88	260	96	75·5	91·8	·024
12·56	255	118	79·5	96·1	·026
12·88	258	168	82·9	99·3	·028
Mean 12·67	262				

When the amount of air dissolved is plotted against the time, the points

lie as shown in figs. 1 and 2, and it will be seen that they are in fair agreement with a logarithmic curve. Hence the results of these experiments can be dealt with in a similar way to that used in previous papers.

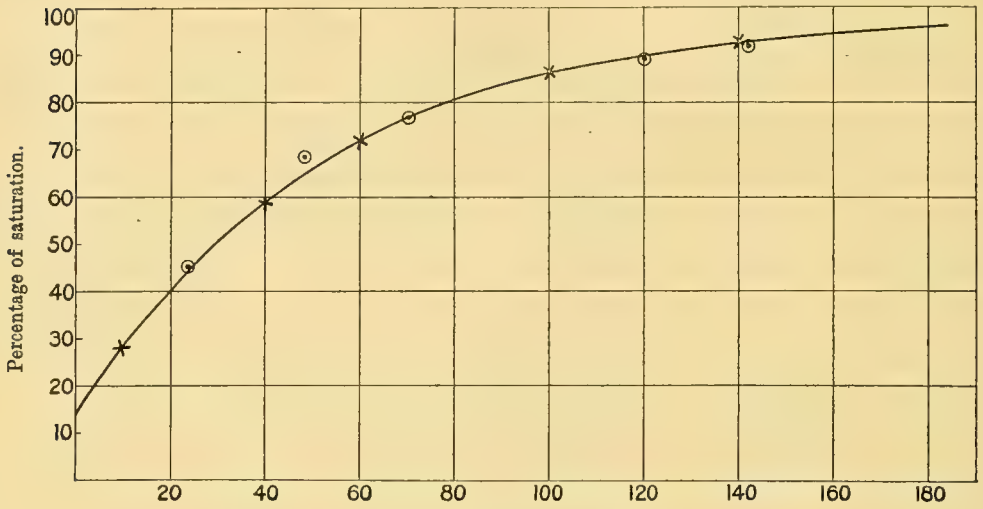

Fig. 1.—Results of experiments with tap-water.
Equation of this curve:—$w = (100 - w_1)(1 - e^{-\cdot 0186t})$.

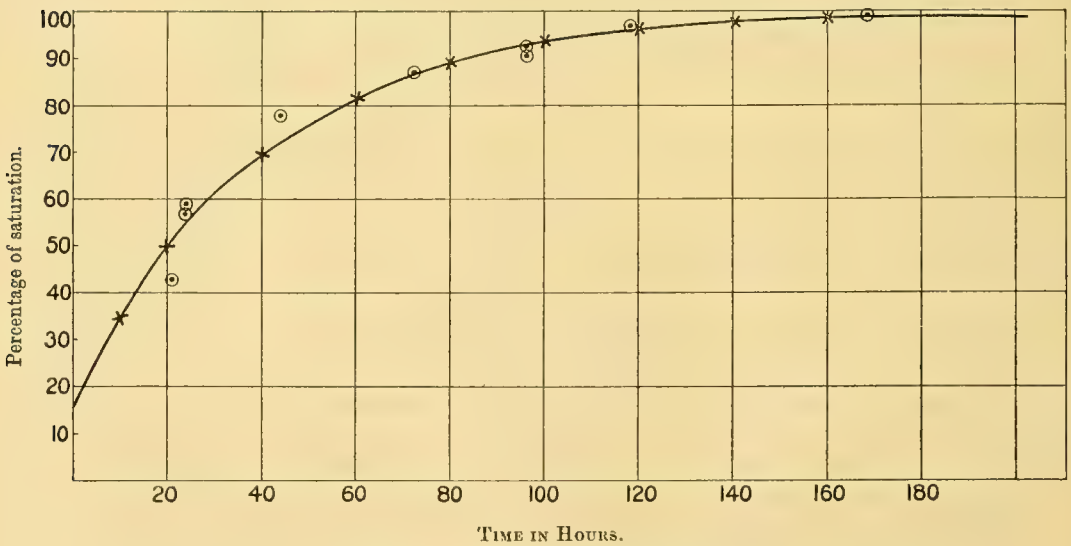

Fig. 2.—Results of experiments with sea-water.
Equation of this curve:—$w = (100 - w_1)(1 - e^{-\cdot 025t})$.

The phenomenon has been shown to take place in accordance with the general equation

$$\frac{dw}{dt} = SAp - f\frac{A}{V}w,$$

where w = total quantity of gas in solution at any moment,

S = initial rate of solution per unit area,

A = area of surface, p = pressure of the gas,

f = coefficient of escape of the gas from the liquid per unit area and volume,

V = volume of liquid.

This can be written

$$\frac{dw}{dt} = a - bw, \text{ where } a = SAp \text{ and } b = f\frac{A}{V},$$

that is, the values of the constants under the conditions of the experiment. The values of the b constant have been calculated for each experiment, and are given in the last column of Tables I and II. It will be seen that the experimental values obtained approximate to a constant; the deviations apparently indicate the magnitude of the experimental errors.

The values of b for the curves shown in figs. 1 and 2 are:—

For tap-water b = ·0186.
For sea-water b = ·0250.

These values may be taken as the mean values of the b constant for the conditions of area and volume obtaining in the experiments. In order to compare the results of these experiments with those to be described it was necessary to reduce the constant to unit area and volume, and in order to do this, it was assumed that in this case, as in the case of the experiments described in previous communications, the rate of solution varied with the area exposed and inversely as the volume.

Since $f = \frac{bV}{A}$, the value of f was calculated in each case.

In the case of tap-water A was = 12·62 sq. cm. and V = 258 cc.; hence f = ·388.

In the case of sea-water A = 12·67 sq. cm. and V = 262 cc.; hence f = ·509.

These values are an index of the rate of solution when a small body of partially de-aerated water is exposed to the air, in a quiescent condition, and kept at as uniform a temperature as possible.

There was reason to think that the irregularity which was noticed in these experiments might have been due to changing atmospheric conditions,

particularly the humidity of the atmosphere. In order to verify this point a further experiment was made.

The effect of the humidity of the air in contact with the water on the rate of solution is shown by the following experiment:—

Four tubes, each 320 mm. long and 40 mm. diameter, were placed in a thermostat after being filled with de-aerated water. Three of these tubes, after 50 cc. water had been withdrawn from each, were then connected by means of rubber corks and glass tubing, so that a current of air could be drawn through the series. The fourth tube was left open to the atmosphere.

Unfiltered air was drawn through the air-space of tube 1, and then through two *U*-tubes containing calcium chloride, from which the dried air passed into the air-space of tube 2, whence it passed directly into the air-space of tube 3. Thus the air in tube 2 was much drier than that in the atmosphere; and that in tube 3 was more moist, and probably nearly saturated with aqueous vapour.

The results are given in the following table:—

TABLE III.

Experiment with air of different degrees of humidity.

Temperature of Experiment, 15° C.

No. of tube.	Area.	Vol. of water.	Time of exposure.	Degree of aeration.	Value of *b*.	Value of *f*.
1	12·56	340 c.c.	43 hrs.	41·5 %	·0125	·34
2	12·25	323	44	63·2	·023	·61
3	12·25	327	44·5	31·3	·009	·23
4	12·25	370	42	32·7	·010	·29

It should be noted that tube 4 was exposed in the middle of the thermostat at a time when the humidity of the air was considerable. Hence the value *f* is rather low.

On examining these results it will be noticed that the tube through which the dried air was drawn shows the largest proportion of dissolved air, although the time of exposure was practically the same in each case. In fact, the figures show that the water in this tube absorbed more than twice as much air as that in the tube through which the moist air was drawn.

In order to reduce these experiments to a basis which will allow comparison with the previous experiments, the values of f have been calculated in the usual way, assuming that the process of solution in this case is the same as before. These values of f are given in the last column of Table III, and on comparing them with the values already deduced for tap-water and sea-water some interesting relations become evident.

It will be seen that the value of f for the tube through which undried air was drawn is approximately the same as that derived for tap-water from previous experiments, but the value for the tube with the dried air is very much greater, and that for the tube with the air saturated with aqueous vapour is very much less than the mean value. This shows that when the air above the water is very dry the absorption of atmospheric gases takes place very much more rapidly than usual.

On the other hand, when the air is saturated, or nearly saturated, with aqueous vapour the rate of solution is very greatly retarded. This would seem to indicate that the process by which the dissolved gas is carried down into the body of the liquid is affected by evaporation from the surface of the liquid, since the evaporation will be at a maximum when the air is dry, and a minimum when it is moist.

In considering, therefore, this question of the mechanism of solution, there are two factors which, whatever others may affect it, are obviously of primary importance, namely: (1) concentration of dissolved salts in the surface-layers due to evaporation; (2) cooling of the surface-layers produced by evaporation.

Both these factors are of such a nature as to result in an increase of density of the surface-layers, which would tend to set up vertical currents in the body of the water. In the case of waters containing large quantities of dissolved salts, the concentration of these salts by evaporation must play a very important part in the process of solution of air. In this connexion it is important to notice that the rate of solution of air by quiescent bodies of sea-water may be much more rapid than that by similar bodies of fresh water, as shown by the relative magnitudes of the values of f in each case.

In the case of water containing only small quantities of salt in solution the effect of concentration would not be so great, but would probably be of somewhat the same magnitude as the effect produced by the cooling of the surface layers. This cooling will, of course, result in an increased density of the surface layers, provided the temperature is not below 4°C., and consequently it will in most cases operate in such a way as to hasten the process of solution.

These two factors, tending as they do to set up a slow circulation from the

surface to the bottom of a mass of water, must be of much greater importance than diffusion, which is such an extremely slow process that months are required to detect its action even in the laboratory. This is further indicated by the fact that, to examine the effects of true diffusion experimentally, it would be necessary to take great care to maintain an absolutely uniform temperature, and to protect the column of water under observation from any external agency which might result in producing currents in the water.

The experiments so far discussed have been made with very shallow depths of water not more than about 260 mm. from the surface. It is, of course, necessary to extend them in order to investigate the question as to what depths mixing is appreciably induced by the conditions brought about by the evaporation from the exposed surfaces of quiescent waters, fresh or salt, under laboratory conditions. But such experiments would require observations to be carried on for very long periods of time, and very great care would be necessary to ensure uniformity in the conditions affecting evaporation during their continuance. The authors have not hitherto had time or opportunity of carrying out such experiments, but it is hoped to commence some experiments of this kind in this College next session.

A number of preliminary experiments have been made by one of the authors with columns of water of from 18 to 24 mm. cross-section,[1] and of such length to allow of observations to be made to depths of about 1800 mm. The results of these experiments prove that mixing induced by evaporation from the exposed surfaces of columns of water does take place down to depths of at least 1800 mm., and that it occurs to a more decided extent in sea than in fresh water. Each of these experiments, however, extended over a considerable number of days, and no precautions were made to keep the conditions of evaporation from the exposed surfaces of the columns of water uniform. The results that were obtained from different experiments were consequently not sufficiently concurrent to determine whether they could be brought within the simple law found for the more shallow depths of water or not.

The following experiment goes to show that the concentrated layers of salt solution, which result from evaporation at the exposed surface of a de-aerated column of sea-water, stream downwards, as they are formed, with little or no tendency to dissipation of their dissolved air-content in lateral directions.

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[1] See "Unrecognized Factors in the Transmission of Gases through Water." By W. E. Adeney, Phil. Mag., March, 1905.

For this experiment a double-bulbed tube of the form shown in fig. 3 was employed. The two bulbs *A* and *B* were of 175 cc. capacity each. They were connected by a narrow tube *C*, 6·4 mm. bore and 300 mm. long. The lower bulb *B* terminated in a small draw-off tube *b*, and the upper bulb *A* was continued by the straight tube *D*, about 50 mm. long and 20 mm. bore.

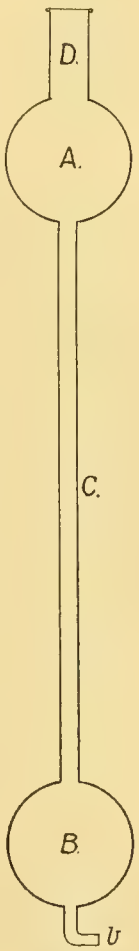

FIG. 3.

The whole tube was exhausted and filled with sea-water, the dissolved gases in which had been previously removed by boiling the water in vacuo, and extracting the gases by means of the mercury pump, described in Part I of this communication. The tube after being filled was securely closed from contact with the air, and placed in a thermostat, kept at the temperature of 12·7° to 13° C.

When the contents of the tube had attained the temperature of the thermostat, the cork was removed, and a little water was drawn out so as to lower the level of the water in the tube to about 20 mm. below the mouth of *D*. The tube was then fitted with a cork, furnished with outlet and inlet tubes, so that a small air space was left above the water in *D*, through which a current of air could be drawn without disturbing the surface of the water. Two weighed calcium chloride tubes were attached to the outlet tube, to absorb the water-vapour brought over from the water in the bulb with the air-current, and to afford the means of determining the weight of water evaporated during the experiment.

A current of air, previously dried by passing through calcium chloride tubes, was drawn through the air-space in the tube for six days. The dissolved air-content of the water in the upper and lower bulbs was then separately determined, with the following results :—

Gases expressed in cc. at N.T.P. per 1,000 cc. sea-water.

	Upper Bulb.	Lower Bulb.
Oxygen,	3·40	2·80
Nitrogen,	6·83	5·43

The initial air-content of the water in the two bulbs may be taken as practically 0.

Sea-water when saturated with air at 13°C. contains per litre :—

Oxygen,	6·06 cc.
Nitrogen,	11·77 cc.

During the experiment 7·935 grams water were evaporated.

It will be seen from the above figures that, while the water in the upper bulb was only a little more than half saturated, that in the lower bulb was also very nearly half saturated. That is, the air-content of the water was practically uniform, although the surface layer was not saturated. And the figures consequently prove that, while the dissolved gases were freely drawn down the connecting tube into the lower bulb by gravitation, they showed no tendency to spread in lateral directions in the upper bulb during their downward passage through it.[1]

The authors desire again to express their indebtedness to Dr. Hackett for the interest that he has continued to take in their investigation of the subject of this and previous communications.

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[1] See Phil. Mag., March, 1905.

SCIENTIFIC PROCEEDINGS.

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Vol. XVI. (N.S.), No. 14. DECEMBER, 1920.

A DETERMINATION, BY MEANS OF A DIFFERENTIAL CALORIMETER, OF THE HEAT PRODUCED DURING THE INVERSION OF SUCROSE.

BY

HENRY H. DIXON, Sc.D., F.R.S.,

UNIVERSITY PROFESSOR OF BOTANY IN TRINITY COLLEGE, DUBLIN;

AND

NIGEL G. BALL, B.A.

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A DETERMINATION, BY MEANS OF A DIFFERENTIAL CALORIMETER, OF THE HEAT PRODUCED DURING THE INVERSION OF SUCROSE.

By HENRY H. DIXON, Sc.D., F.R.S.,
University Professor of Botany in Trinity College, Dublin,
AND
NIGEL G. BALL,[1] B.A.

[Read November 23; published December 14, 1920.]

Very little attention seems to have been paid to the heat changes accompanying enzyme reactions. Theoretically these can be deduced from the difference in the heats of combustion of the initial substances and the products of the reaction; but, as Brown and Pickering (1) have pointed out, such methods are inaccurate, as the amounts of the thermal changes to be measured are so close to the limits of experimental error for the combustion values.

For example, in the case of inversion of sucrose, using the values for the heats of combustion obtained by Stohmann and Langbein (2), we get—

Sucrose	1352·7	cal. per gm. mol.	
Dextrose . . 673·7	1349·6	„ „ „	
Laevulose . . 675·9			
Difference	3·1	cal. per gm. mol.	

From this it would appear that the heat of inversion of sucrose in the solid state is + 3·1 cal. per gm. mol., or + 9·1 small calories per gram inverted. This value represents only about 0·1 per cent. of the sum of the quantities measured in order to determine it, and little reliance can be placed upon its accuracy. In order to determine the heat of inversion in the dissolved condition, this value must be corrected for the differences in the heats of solution of the substances concerned, and, when this is done

[1] Mr. Ball is indebted to the Department of Scientific and Industrial Research for a maintenance grant which was received during the progress of this research.

the value + 9·1 cal. becomes, according to Brown and Pickering, − 1·0 cal. per gram of sucrose inverted. By direct experiment Brown and Pickering obtained the value + 11·2 cal. per gram inverted. In view of the difference between this result and that deduced from the heats of combustion, it seemed to us desirable to make a fresh determination of this value, using a direct method. The energy changes due to enzyme action are of interest in connexion with the study of the chemical changes which take place in the plant as a result of photosynthesis.

In the experiments of Brown and Pickering ordinary calorimetric methods were employed, and the temperature was measured by means of a sensitive mercury thermometer. As the temperature changes which have to be measured are very small and take place with comparative slowness, we decided that a differential method, using vacuum flasks and a sensitive thermocouple, constructed on the lines of those employed in cryoscopic measurements (Dixon (3)), would be suitable for the purpose. After our apparatus had been set up and used for some preliminary experiments, we became acquainted with the work of A. V. Hill (4), in which a somewhat similar type of apparatus was used in certain physiological experiments. In his paper is given a clear discussion from the mathematical standpoint of the characteristics and advantages of the differential method, which it is unnecessary to repeat here. The essential features of the method as employed by us to determine the thermal changes due to enzyme action will, however, be briefly explained, followed by a description of our apparatus.

Two similar vacuum flasks are used, each containing one junction of a thermocouple, which is connected through a reversing switch with a sensitive galvanometer. The deflection of the galvanometer is directly proportional to the difference in temperature of the two flasks. If each flask contains the same quantity of liquid and has the same coefficient of conductivity, the changes in external temperature will affect them both to the same extent, and the differential temperature will remain the same. If heat is produced in one flask, the increase in the galvanometer deflections will be directly proportional to the rise in temperature, and the radiation correction will be proportional to the galvanometer deflections, and will be unaffected by changes in the temperature of the surroundings.

Changes in temperature due to dilution of the sugar solution by the enzyme solution in the experimental flask can be neutralized by allowing a similar dilution (using an enzyme solution which had previously been heated to 100° C.) to take place in the control flask.

Construction of Thermocouple.

The thermocouple employed was constructed of copper and eureka wires, according to the method previously described (3), with the exception that the wires leading to the junctions passed through narrow glass tubes instead of being fastened to pine rods. The glass tubes used were 25 cm. long, and the wires, which were well coated with collodion varnish, projected about 1 cm. from the lower ends. The junctions were protected from injury by being attached to little pieces of wood which were pushed into the tubes. The remaining spaces in the tubes were filled with paraffin-wax, which effectually sealed them and kept the wires in place. The copper wires of the thermocouple then passed to the reversing switch of the type already described (3). This switch is preferable to a mercury one, owing to complete absence of thermoelectric effects.

The galvanometer used was of the Ayrton-Mather pattern, giving for one micro-volt a deflection of the spot of light on the screen one metre distant from the mirror, of 10 mm., and for one micro-ampere 206 mm. By means of the reversing switch, readings were always taken on both sides of the middle of the scale, and subtracted from one another to obtain the deflection. This ensures that errors due to movement of the zero or to thermoelectric effects at the junctions of the leads with the galvanometer terminals, are completely eliminated.

Calibration.

The thermocouple was calibrated by using it for the determination of the freezing-point of a solution of sucrose of definite concentration, according to the method previously described (3). As the depression of freezing-point of solutions of sucrose of different concentrations are known from the researches of Raoult (5), this affords an easy and accurate method of calibration.

The thermocouple used was found to give a deflection on the scale of 1 mm. per 0·00258° C.

Method of Releasing Enzyme Solution.

It is obviously essential that the enzyme solution, at the moment of mixing, be at exactly the same temperature as the solution on which it is to act. This can only be ensured by having it in a container immersed in the solution for some time before the commencement of the experiment. It is also necessary that the mixing be performed without opening the flasks, which might cause a disturbance in temperature of the liquids contained in them. In Brown and Pickering's experiments (1) the enzyme solution was contained in a glass pipette, the end of which was bent upwards and then

downwards. This was immersed in the solution in the calorimeter. By means of a combined force and suction-pump, the enzyme solution was forced out of the pipette, and then the pipette was washed out by drawing in some of the mixed liquid and again expelling it. As this method was

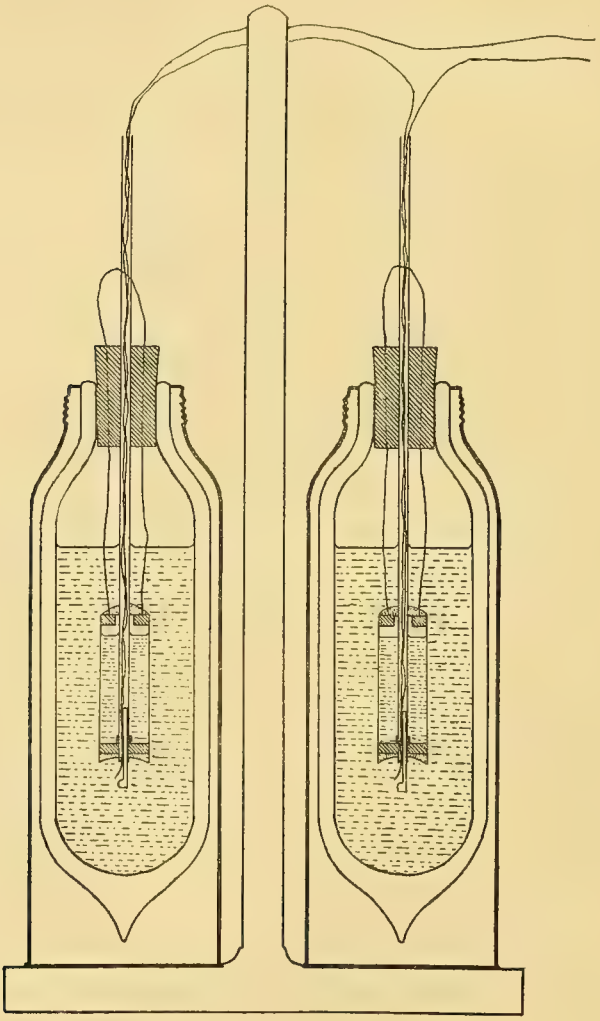

Fig. 1.

unsuitable for use with our apparatus, owing to the narrow necks of the vacuum flasks, we decided to enclose the enzyme solution in a capsule of paraffined paper, attached to one of the glass tubes of the thermocouple, a similar arrangement being used in the control flask (see fig. 1). These

capsules, which were found to be quite satisfactory, were constructed in the following manner :—

About 1 cm. from the lower ends of the glass tubes containing the wires of the thermocouple little copper bands were cemented to the glass with Canada balsam, in order to support the lower ends of the capsules. The upper and lower ends of the capsules were formed of discs of cork 2 cm. in diameter. The lower ones were perforated by holes, into which the glass tubes fitted tightly. The upper ones had holes sufficiently large to allow the copper bands to pass through, and to these discs silk threads were attached, for the purpose of rupturing the capsules. Cylinders, 6 cm. long, which fitted tightly on the cork discs, were made of a double thickness of paper, with the edges cemented with seccotine. The upper ends of the paper cylinders were notched and turned over on the upper corks, leaving the lower ends open. The cylinders were then immersed in melted paraffin-wax, and the beaker which contained it was placed under the receiver of an air-pump, which was then exhausted. This removes all air-bubbles from the paper, and ensures that it is thoroughly impregnated with wax. The capsules were then removed, and allowed to cool. In order to assemble the capsules on the tubes of the thermocouple, the tubes were passed through the holes in the upper corks, which were now firmly attached to the paraffined paper. The lower corks were then pushed on to the tubes until they came into contact with the copper bands, and the edges of the discs were smeared with vaseline. The open ends of the capsules were then pushed over the lower cork discs until the ends of the paper capsules projected about 0·5 cm. The whole thermocouple was then inverted, and the cup-shaped space left below the lower cork was filled with melted paraffin-wax of a low melting point. This effectually seals the lower ends of the capsules. For the purpose of filling the capsules, there is sufficient space between the glass tube and the edge of the hole in the upper cork to insert the end of a small pipette. The capsules used held 15 c.c. of liquid, and, after filling, the hole at the top round the glass tube was sealed with paraffin-wax.

If carefully made, these capsules give no trouble due to leakage, and are easily opened by pulling the silk thread. This separates the paper cylinder from the lower cork, which is held by the copper band, and allows the enzyme solution to mingle rapidly with the surrounding liquid.

Flasks.

The flasks used were the ordinary so-called pint-size vacuum flasks, which are made of silvered glass, enclosed in a metal case. The conductivity constants of the two flasks were found to differ by about 9 per cent. Unless

the two flasks change in temperature at the same rate, owing to alteration in temperature of the surroundings, errors will be introduced should the external temperature change during the course of an experiment. In our later experiments on the inversion of sucrose the external temperature remained constant within about 0·1° C., so that the error introduced was negligible. But owing to the sensitiveness of the temperature measurements, it was found that slight inequalities in the radiation to which the two flasks were exposed gave rise to considerable errors. To avoid this, the apparatus was enclosed in a heavy copper cylinder, covered with a copper lid. This was placed in a wooden cask, and packed around with cork dust.

The water-equivalent of the experimental flask was found to be 9·5 grams.

Radiation Correction.

The radiation correction was found to be affected very largely by the method adopted for stirring the flasks. In our earlier experiments the glass tubes of the thermocouple, with the capsules attached, passed loosely through holes in the corks which closed the necks of the flasks, and were attached to a cross-piece which was free to slide on a vertical rod between the two flasks. A light piece of cane was attached to the cross-piece, and passed through a hole in the copper lid of the containing vessel. By this means the thermocouple and capsules could be moved up and down, thus stirring the liquid in the flasks.

This method of stirring suffers from the disadvantage that the radiation error is very greatly increased owing to loss of heat from the wet surfaces of the tubes when they come out of the flasks, and was therefore abandoned. The method finally adopted was to clamp the glass tubes between split corks in the necks of the flasks, and to effect the stirring by shaking the flasks. The cask containing the apparatus was slung in a horizontal position from a bar of wood which rested on a central pivot, and could thus be rocked backwards and forwards. By this means the rate of cooling during stirring was decreased to less than one-third of its former value.

The correction for radiation was then determined. In a preliminary experiment 315 c.c. of water, at about 90° C., was put into each flask, and a sensitive thermometer inserted through the cork which closed the neck. The flasks were then placed in a shaking-machine, and the rate of cooling determined. Assuming Newton's Law of Cooling, the rate of cooling at any temperature = the excess of that temperature over the surroundings × a constant. This constant, which we may call k, was calculated from the formula :—

$$-k \log e = \frac{1}{t} \log \left(\frac{T - T_0}{A - T_0} \right),$$

where A is the initial temperature, T the final temperature, T_0 the temperature of the surrounding air, and t the time in hours during which the temperature falls from A to T. It was found that the rate of cooling of one flask was slightly greater than that of the other, but, as Hill (4) has pointed out, compensation can be made for this by adjusting the amounts of liquid in the two flasks. By putting 315 c.c. of water in the experimental flask, and 287 c.c. in the control flask, it was found that the rate of cooling was approximately the same in both.

A more accurate determination of the value of k was made in the following manner. The apparatus was set up with the thermocouple in the flasks, the water in the experimental flask being about 1° C. warmer than that in the control flask, and the amounts of liquid in the flasks adjusted so as to make their conductivity constants approximately equal, i.e. 315 c.c. in experimental flask and 287 c.c. in the control. The rate of cooling was determined by noting the decrease in the galvanometer deflections during different periods of more than one hour while stirring was carried on, and the constant k was calculated from the formula. In this case the rate of cooling at any instant is proportional to the deflection of the galvanometer, and therefore A and T are equal to the initial and final deflections respectively, and T_0 is equal to O. The value of 0·05 for k was obtained as the mean of a number of concordant observations. This means that at any temperature the rate of cooling per hour was 5 per cent. of that temperature. The smallness of the correction for radiation losses clearly demonstrates the value of this apparatus for the determination of the amount of heat produced during a chemical reaction, when the time of the reaction is necessarily prolonged.

Determination of the Heat Produced during the Inversion of Sucrose.

The sucrose solution which was used contained 100 gm. per litre of solution. Both experimental and control flasks were charged with 300 c.c. of this solution. As the temperature during the experiment could be kept constant, the same quantity of liquid was used in each flask. The solution of invertase was prepared according to Davis' (6) method. In one capsule was put 15 c.c. of the enzyme solution, and in the other 15 c.c. of the same solution which had been previously heated to 100° C. After the capsules had been sealed, the thermocouple was inserted into the flasks, which were then corked with the split corks. The silk threads passed out through grooves between the two halves of the corks. If the corks and threads are well greased, no leakage from the flasks occurs.

The diagram (fig. 1) shows the arrangement of the thermocouple and flasks when assembled.

The apparatus was then set up and left overnight in order that the temperature inside the capsules might become the same as that of the surrounding liquid. The next morning the deflections of the galvanometer were observed at intervals, and, if constant, the capsules were ruptured and the experiment started. The fact that the deflections are constant before the commencement of the experiment is a proof that no leakage of the enzyme solution has taken place. The deflections were observed at regular intervals while the apparatus was continually shaken. When it was desired to stop the

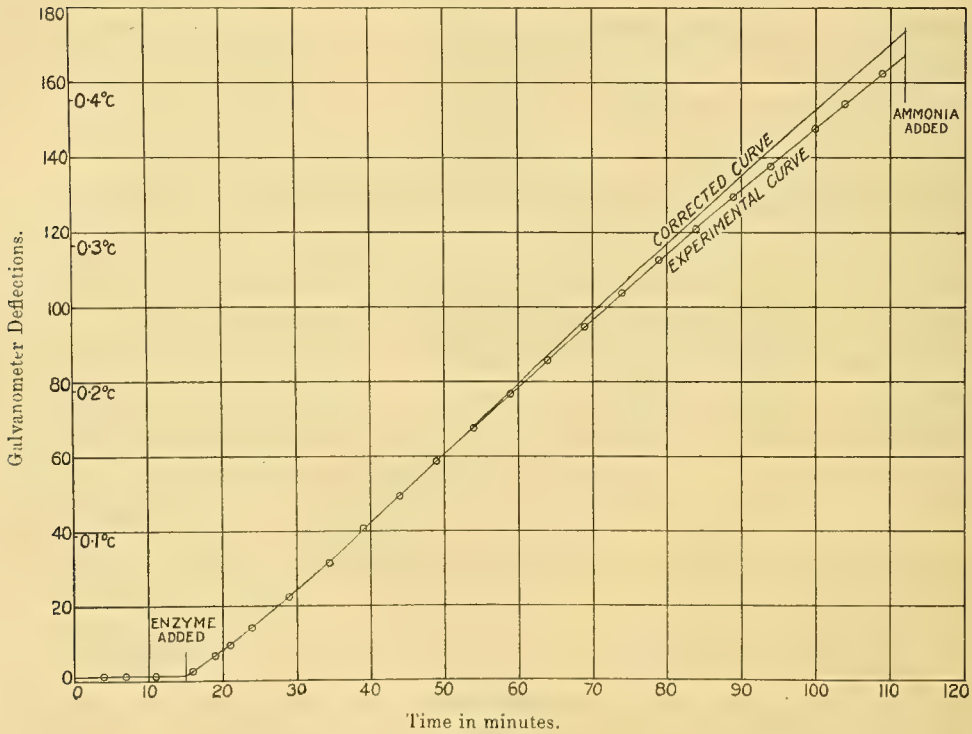

Fig. 2.

inversion, the experimental flask was rapidly opened, and 10 c.c. of ammonium hydrate run in. The exact time at which this took place was noted.

The amount of sucrose inverted was determined by measuring the reducing power of the solution according to Pavy's method.

A curve showing the rise in temperature was plotted, and by extrapolating this curve the exact temperature at the moment at which inversion was stopped can be deduced. From this curve another curve corrected for radiation losses was drawn, according to the method described by Hill (4).

The curve obtained in Exp. No. 7 is reproduced in fig. 2. It will be

noticed that the temperature rises steadily from the moment mixing takes place, and after the correction is made for radiation losses the curve is very nearly a straight line throughout the course of the experiment. This is probably due to the fact that the sucrose is largely in excess of the enzyme, so that the rate of the reaction is not sensibly diminished even after about 40 per cent. of the sucrose has been hydrolysed.

In calculating the results, a correction is applied for the difference in the specific heat of the sucrose solution used from that of water, and also a correction for the very slight reducing power of the sucrose and invertase solutions.

The results of our two final experiments are shown below. The temperature of the solution during both these experiments was about 10° C. The values obtained in earlier experiments are not given, as, owing to the method of stirring adopted, the radiation error was very large and uncertain, and therefore the results were unreliable.

No. of Expt.	Time of Expt.	Amount of Sucrose inverted.	Percentage of Sucrose inverted.	Rise in Temperature.	Radiation Correction.	Gm. cal. per gram inverted.
6	95·5 mins.	12·98 gm.	43·3 per cent.	0·4383° C.	0·0167° C.	11·20
7	97 mins.	12·62 gm.	42·1 per cent.	0·4274° C.	0·0173° C.	11·27

The radiation correction in Expt. 6 is slightly smaller than in Expt. 7, although in the former case the rise in temperature was greater than in the latter. This is due to the fact that, at the commencement of the experiments, the experimental flask was slightly cooler than the control in Expt. 6, and slightly warmer in Expt. 7.

The values, 11·20 and 11·27, obtained in our experiments agree well with the values, 11·28 and 11·13, given in Brown and Pickering's paper, and the mean of all these, 11·22, may be regarded as a reasonably accurate estimate of the number of calories evolved per gram of sucrose when inverted in solution by means of invertase. This is equal to 3·83 calories per gram molecule.

Since these experiments have been concluded, the results obtained by Barry (7 and 8) on the heat of inversion of sucrose by hydrochloric acid have been published. In this case a value of + 10·4 cal. per gram inverted at 20° C. was obtained. It seems possible that the discrepancy between this value and that obtained in our experiments is due to the fact that the energy-changes

in the acid solution are different from those in a neutral solution. Barry himself has shown that the heat of solution of sucrose in acid is different from that in water.

The Hydrolysis of Maltose.

We also made some attempts to obtain a value for the thermal changes which take place when maltose is hydrolysed to dextrose under the influence of maltase. According to Stohmann and Langbein (2), the heat of combustion of maltose hydrate is 1339·8 cal. per gm. mol., and for two gm. mol. of dextrose it is 1347·4. This would give a value of – 7·6 cal. per gm. mol. for the hydrolysis of maltose, but such indirect determinations are of little use.

The direct determination of this value is attended by many difficulties. At air temperature maltase acts very slowly, and even at the optimum temperature, about 38° C., the action is still rather slow. A 5 per cent. solution of maltose when acted on overnight by one-twentieth of its volume of extract of dried brewers' yeast at 38° C. was only hydrolysed to the extent of about 42 per cent. An attempt was made to obtain a value for the thermal changes accompanying hydrolysis by filling the flasks with a 5 per cent. solution of maltose at 38° C., and using an extract of dried yeast as a source of maltase. A curve showing the change in the galvanometer deflections during 1½ hours was plotted, and then the capsules were ruptured. Any thermal changes produced by the action of the enzyme on the maltose should cause a change in the direction of the curve. No change was noted, but after 1½ hours the amount of hydrolysis, when determined by the polarimeter, was so small as to be within the limits of experimental error, and so no conclusions could be drawn.

In order to obtain accurate results it would be necessary to obtain a much more active preparation of maltase, and to have a pair of flasks so carefully adjusted that, when filled with a sugar solution at 38°C., the temperature of the two fell at exactly the same rate. This would ensure that any change in the deflections of the galvanometer was entirely due to the action of the enzyme.

Summary.

Estimations of the thermal changes due to the action of enzymes when obtained from the heats of combustion are inaccurate, as the values obtained are so close to the limits of experimental error for the heats of combustion values.

A differential calorimeter, in which the temperature is measured by means of a thermocouple, was used for the determination of the heat produced by the action of invertase on sucrose.

A value was obtained which agrees closely with that previously given by Brown and Pickering. The mean of all the results is 3·83 cal. per gm. mol.

Attempts to obtain a value for the heat of reaction during the hydrolysis of maltose have not yet been successful.

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BY

JOHN J. DOWLING, M.A., F.Inst.P.;

AND

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(In conjunction with the late Prof. J. A. McClelland, F.R.S.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XV.

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Smithsonian Inst. MAR 21

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Somewhat similar methods have been employed by other workers, and our aim has been to examine what degree of accuracy the method was capable of when applied to measure the shortest time-interval we could reproduce with sufficient accuracy. It was, furthermore, desirable that the apparatus should be kept as simple as possible, in view of the possible application of the method in the workshop or testing room. We had intended to test the application of the method to the measurement of the velocity of explosion in explosives, but this part of the investigation was not carried out. References to previous work have been fully given by Klopsteg[2] in a recent paper, and need not be repeated here; while the results of a similar investigation to ours were published by Webster,[3] and came to our notice in the last issue of Science Abstracts.

The particular method employed is based on the charging of a condenser from a battery of steady e.m.f. through a non-inductive resistance. The charge q acquired during t seconds is given by:—

$$q = q_0\left(1 - e^{-\frac{t}{RC}}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or,
$$t = 2{\cdot}3\ RC[\log q_0 - \log (q_0 - q)] \quad . \quad . \quad . \quad (2)$$

or, approximately,
$$t \doteqdot \frac{RCq}{q_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] The problem was submitted to us by Messrs. Nobel's Explosives Co., and this paper is published with their permission. We desire to express our thanks to the Company and Mr. Rintoul for their courtesy.

[2] Klopsteg: Physical Review, xv, 7, 12. 1920.

[3] Webster and Allen: Am. Phil. Soc. Proc. 58, No. 6, p. 382. 1919.

To measure times of the order of 100 micro-seconds (100×10^{-6} sec.), if q_0 is to be ten times q, we see, from (3), that the product RC should be about $\frac{1}{10000}$. Having a very well insulated mica condenser of one microfarad capacity, we made R 1000 ohms in most of our observations; but, with a view to testing the method somewhat, we varied R in a few cases. The actual values of R and C required are to some extent determined by the sensitivity of the galvanometer, but the battery e.m.f. can also be modified so as to give q and q_0 suitable values. To measure q_0 and q a ballistic galvanometer with a universal shunt was employed, so that large, and nearly equal, deflections were obtained for both q_0 and q. An eight-volt battery was employed throughout, and the galvanometer had a ballistic sensitivity of about 450 scale divisions per micro-coulomb.

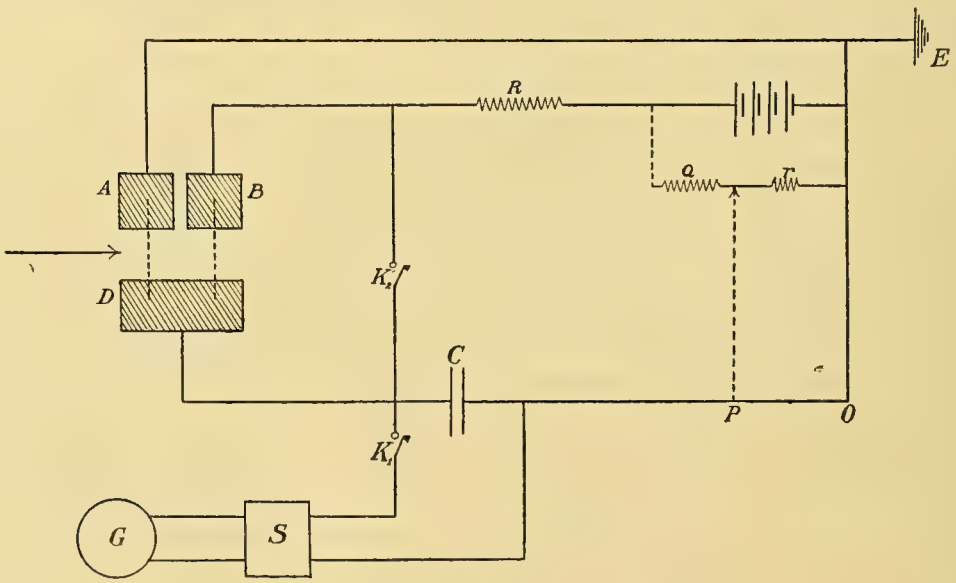

Fig. 1.

The main difficulty to be overcome in practice is the means to be adopted by which the condenser is caused to commence and cease charging at the beginning and termination, respectively, of the time interval to be measured. In order that accidental and constant errors should be reduced to a minimum, it is necessary to have the commencement and termination of the charging brought about by two operations as similar as possible. We attempted to do this by arranging that these operations should each consist in the breaking of fine copper wires, in which practically the same currents would be passing. These are shown in the diagram (fig. 1) by the dotted lines. The wires were soldered to the brass plates (A, B, D), and care was taken to have them under

practically the same degree of tension before soldering. These were broken in turn by a small (·22) rifle bullet travelling in the direction of the arrow, and the velocity of this bullet was measured immediately afterwards by an independent method. Check observations showed that the wires produced no appreciable retardation of the bullet. In the experiments the wires were never mounted closer than 2 cms. apart, so that the slightly different lateral displacements which occur before breaking should not seriously affect the result.

The bullet velocity was determined as follows:—Two circular discs of cardboard, about two feet in diameter, were mounted about two feet apart, one at either end of a stout shaft, turning between centres, and driven by a powerful electric motor at a speed of about 35 revolutions per second. To these discs somewhat larger thin paper discs were pasted, and the whole apparatus mounted so that the bullet, travelling parallel to the axle, would pierce the two paper discs in succession near their edges. A resistance in the motor circuit allowed the speed of the discs to be adjusted to a constant steady rate indicated by a stroboscope arrangement. The shot was then fired, and from a measurement of the angular displacement of the bullet holes, relative to each other, the bullet velocity could be determined. Certain obvious check experiments were carried out to determine whether, for instance, the bullet was appreciably retarded or deflected sideways during its passage through the first disc. The angle to be measured was generally about 30°, and an error of more than one or two per cent. was unlikely.

The apparatus was connected up as shown by the *full lines* in the diagram. (The dotted lines P, Q, r refer to a modification referred to later.) Observations were conducted as follows:—Having measured the separation of the wires in position, and both keys K_1, K_2 being open, the motor speed was regulated until the standard speed of rotation of the discs was reached. The gun was immediately fired, breaking the wires A and B. The shunt being set to unity, K_1 was closed and the deflection observed for q. To obtain the reading for q_0, K_2 and K_1 were then operated in succession, the shunt having been set back to '10.' The observations of the angular displacement of the bullet holes in the discs were finally taken by means of a protractor attached to the axle, the punctures being sighted in turn through the rifle barrel. The following table contains the results of twelve consecutive readings obtained in this manner.

In all cases rate of rotation is 34·5 revolutions per second, and distance apart of paper discs 54·8 cms.

TABLE I.

Angle between bullet-holes in discs.	Velocity of bullet (metres / sec.).	Distance between wires (cms.)	Time interval calculated (micro-seconds) (t_1).	Deflection × shunt ratio for q_0.	Deflection for q.	Resistance R (ohms).	Time interval, measured electrically (micro. sec.) . (t_2).	$(t_1 - t_2)$ = actual "error."	$\frac{100 \cdot (t_1 - t_2)}{t_1}$ = error per cent.
1	2	3	4	5	6	7	8	9	10
28°	242	1·966	80·9	3630	257	1000	79·0	+ 1·9	2·4
27¼°	249	1·910	76·8	3630	261	,,	74·5	+ 2·3	3·1
29°	234	1·900	77·8	3650	264	,,	75·4	+ 2·4	3·2
30°	226	1·762	77·8	3650	264	,,	75·4	+ 2·4	3·2
28½°	238	1·790	75·0	3650	486	500	71·4	+ 3·6	4·8
29°	234	1·894	80·9	3650	515	,,	76·5	+ 4·4	5·4
27°	252	1·980	78·6	3650	144	2000	80·5	− 1·9	2·4
28½°	238	1·949	81·6	3620	149	,,	84·0	− 2·4	2·9
28°	242	1·834	75·5	3620	132	,,	74·2	+ 1·3	1·7
28½°	238	1·816	76·1	3620	132	,,	74·2	+ 1·9	2·5
27¼°	249	1·872	75·0	3600	129	,,	72·9	+ 2·1	2·8
26°	261	1·882	72·0	3600	127	,,	71·7	+ 0·3	0·4

Some further experiments were carried out with a view to reducing the time interval to a still smaller value. It is not possible to do this simply by mounting the wires closer together in the arrangement just described. It would seem that a great part of the percentage error of the above results is due to unequal stretching of the wires before breaking, and, of course, this effect becomes more and more important as the separation of the wires is diminished. To avoid this, several modifications were considered, and one was tried which appeared promising. Unfortunately, the work had to be abandoned before many observations with it had been carried out.

In this arrangement, instead of breaking the wires, the bullet was caused to strike them in such a manner as to *lift* them from two metallic supports, thereby breaking the circuits. The wires were *subsequently* broken by the bullet, but the breaking bore no part in the actual operation of the apparatus.

Each wire was stretched between two spring clips (*aa*, fig. 2), about 3 cms. apart, mounted on a rectangular piece of thin ebonite (*b*). Midway between the clips a large hole was pierced in the ebonite. On either side of this hole lay two stout copper wires fixed to the ebonite, and across them the fine wire (*d*) was stretched, and pressed lightly on them at the points of contact. One of these was then clamped over the other, so that the wires (*d*) were at right angles, small-distance pieces of ebonite being interposed, and the distance between the wires (*d*, *d*) was measured by a microscope with a vertical micrometer motion. The arrangement was then carefully mounted

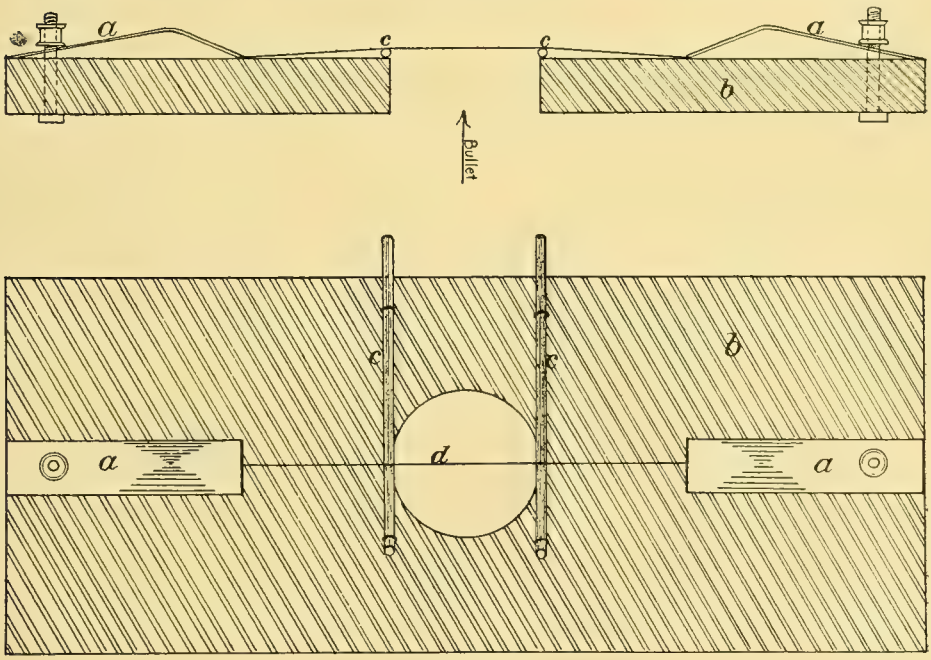

FIG. 2.

so that both wires (*d*) were in the line of fire, and connexions made from the support wires (*c*, *c*) to the electrical apparatus. On either block one of the wires (*c*) corresponded to *A* or *B* respectively, while the other one of course took the place of *D* in the original arrangement. One difficulty was found, but was easily met. Owing to the resistance introduced at the points of contact (*c*, *d*), there is a noticeable drop in potential across the gap (*AD*). This had to be balanced across the condenser, and a potential-dividing arrangement *PQr* was substituted for the former direct-earth connexion shown at *O* (fig. 1). With this refinement, some few observations were made which indicated that measurements of intervals of about 40 micro-seconds

could now be made with about the same percentage accuracy as obtained for the larger intervals given in Table I.

A great part of this work was completed more than a year ago, but the hope that it would be possible to push the investigation to still shorter intervals caused publication to be held back. It appears, from our own experience, and in view of the investigations of Klopsteg and of Webster already mentioned, that the "capacity" methods of measurement for short time intervals can be relied on under favourable conditions to measure to, at least, the nearest micro-second. In our first arrangement larger errors than this occurred, but the improved mounting seemed to promise readings having this accuracy. Under extremely favourable conditions, and using some special apparatus, Klopsteg reduced the errors to one-tenth of this.

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A VIBRATING-FLAME RECTIFIER FOR HIGH-TENSION CURRENTS.

BY

JOHN J. DOWLING, M.A., F.Inst.P.;

AND

J. T. HARRIS, B.Sc.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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By JOHN J. DOWLING, M.A., F. Inst. P.;
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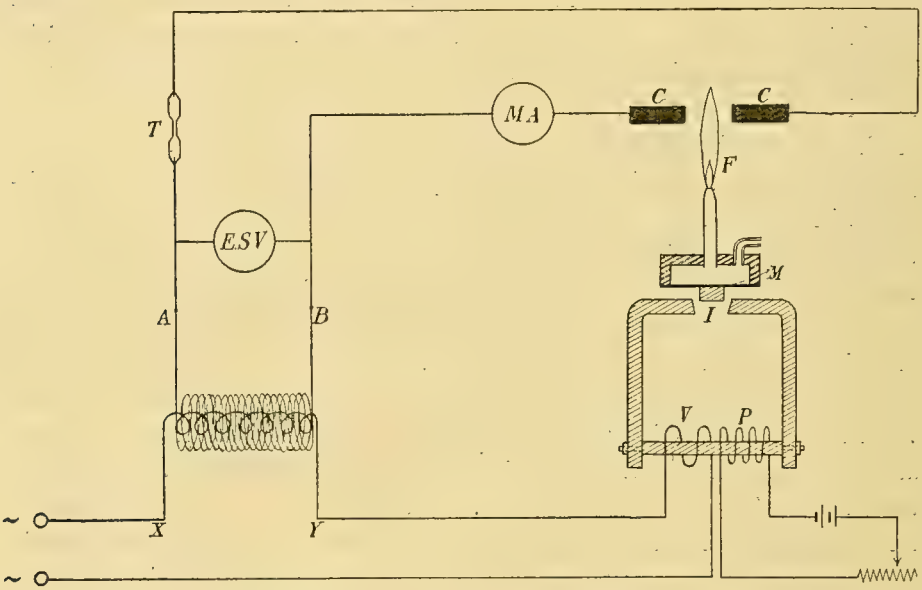
[Read December 21, 1920. Published February 21, 1921.]

Incomplete rectification of an alternating high-tension current can be effected by placing a small flame near one electrode of a spark-gap in the circuit. The unilateral conductivity of this arrangement is due to the large supply of negative carriers of high mobility derived from the flame. It occurred to one of the authors that, by causing the flame to vibrate in synchronism with the pulsations of electromotive force, a supply of ions would then be made available when the e.m.f. was directed in one sense through the circuit, while there would be practically none available to carry the reverse component of current. Almost perfect rectification would be obtainable in this way. After a few trials, a satisfactory arrangement was devised, the simplicity and novelty of which seem to warrant this description.

From the foregoing outline of the principle it will be clear that the flame-vibrations must be strictly in phase with the high-tension electromotive force, and must so occur that the flame rises and falls once, while the electromotive force makes one complete alternation. These conditions are fulfilled in the following way :—The flame-vibrations are produced by a Koënig's manometric capsule, the membrane of which is either a thin iron plate or an india-rubber diaphragm, to the centre of which a small piece of iron is attached. Mounted close to this is an electromagnet supplied with two independent windings. Through one of these windings the full primary current of the high-tension transformer passes. The other winding carries a direct current from a storage battery, a suitable rheostat being introduced for regulating the current, as described below.

The alternating current alone would cause a pulsation of the manometric flame to occur twice in each complete alternation, since the manometric disc would experience an attraction in whichever way the magnet happened to be magnetized. If the direct current in the other magnet winding be now regulated until its magnetizing effect is almost equal to the maximum value of that due to the a.c. winding, it is clear that the magnetization will no longer undergo periodic reversals, but will, on the contrary, vary between two points on the

upper branch of the hysteresis curve. The most favourable value for this "polarizing" current is best got by trial, the manometric flame being observed in a rotary mirror, and the "polarizing" current gradually increased until the alternate maxima of the flame are seen to disappear. A little adjustment of the relative positions of the magnet and capsule may be required to obtain the largest amplitude in the flame-vibration. The dimensions of the capsule and jet are also very important in this connexion, the best results being obtained when the capsule is rather shallow, so that considerable changes in its volume, and therefore in the gas pressure, result from the movements of the membrane in and out. A jet should be selected such that the flame will



be about eight or ten centimetres high, while the supply-tube leading the gas into the capsule should either be of narrow bore or lightly plugged with cotton wool where it opens into the interior of the capsule. With a capsule of 2 c.c. volume and a jet-tube of about 1 c.c., making about 3 c.c. in all, the rubber diaphragm being about 3 cms. in diameter, we obtain flames oscillating between 1 cm. and 10 cms., the height when not vibrating being about 9 cms.

The application of the device for the purpose of rectifying was tested as follows:—A large (Newton) induction-coil was employed to transform the ordinary town a.c. supply (200 volt, 50 ~.) to about 6,000 volts. In the secondary circuit, as well as the rectifying spark-gap[1] *cc*, were included a small vacuum tube and a d.c. milammeter. The vacuum tube was placed in such a position that the reflected image of it in a fixed mirror was vertically beneath

[1] The flat ends of two stout carbon rods were found most satisfactory for this.

the flame; and a rotary mirror was employed to observe the flame and the image of the tube. On exciting the coil, the vibration maxima of the flame were seen to be strictly in phase with the discharges in the tube; and, on adjusting the polarizing current so as to cut out the intermediate maxima, the corresponding vacuum tube discharges likewise ceased. The milammeter then registered about 20 milliamperes.

With a view to testing the degree of rectification, a suitable oscillograph not being available, the following experiments were tried:—An a.c. milammeter was connected in series with the d.c. instrument already used, and the observations repeated. A rather larger current was indicated by this a.c. instrument, which seemed to point to incomplete rectification. However, an interesting explanation was found for this. Tested in series with d.c. currents, the two instruments read the same; but, having doubts as to the validity of such a test, we tried them again in series with current rendered intermittent by a tuning-fork interrupter (50 ~). It was found that the a.c. instrument read nearly twenty per cent. higher under these conditions. As the conditions are very similar in this test to those obtaining during the rectification experiment, and as the observed discrepancy there is exactly accounted for by this effect, we feel justified in assuming that the inverse current must certainly have been less than $\frac{1}{10}$ milliampere, i.e. less than $\frac{1}{2}$ per cent. of the rectified current.

Our next inquiry was directed to the possibility of using such flame-rectifiers for the purpose of charging condensers to high steady potentials from an a.c. supply. For this purpose it is essential that there should be an exceedingly small inverse current, or, in other words, the resistance of the spark-gap must be very high during the intervals when the flame has dropped to its minimum; were this not so, the condenser would discharge with each reversal of the e.m.f., and might even take up reverse charges.

To attain satisfactory conditions for a test it is necessary in this case to introduce two rectifying devices in the circuit, one on each side of the condenser, for if only one were used there would be an oscillating potential on that plate of the condenser which is connected directly to the coil. For the purpose of maintaining a steady, *average* high potential above earth, only one rectifier is required, the other plate of the condenser and the corresponding coil-terminal being earthed; but under these conditions the readings of an electrostatic voltmeter connected in parallel with the condenser may be misleading. We therefore arranged two rectifying devices, with their a.c. coils in series, and having separate rheostats for controlling their polarizing currents. The two were, of course, arranged to pass high-tension current in the same direction, and were placed respectively in the leads from the coil-terminals to

those of the condenser, a leyden jar of about 90 cms. capacity. Connexions were made from the condenser-terminals by means of wet thread to the Kelvin electrostatic voltmeter. The wet thread possessed a very high resistance, and was employed with a view to testing whether the condenser was actually charged to a steady potential, or if, on the contrary, its potential was alternating. By allowing the flames to vibrate under the influence of the a.c. alone (polarizing current cut off), that is to say, when the condenser-potential was alternating, it was found that the voltmeter reading was zero. On polarizing the magnets, the voltmeter immediately charged up, and showed a potential about the same as that registered when connected directly to the coil. If the insulation of the condenser and voltmeter had been better than they were, we should have expected to obtain perhaps a slightly higher potential, corresponding to the peak value of the high-tension e.m.f.

A somewhat more convincing demonstration of the rectifying property of the device was achieved by using a Braun cathode ray-tube as an oscillograph. A small coil was mounted near the cathode stream, and formed part of the high-tension circuit. With the rectifier functioning, two spots were formed on the fluorescent screen, one being due to the undeflected rays. The other spot was, of course, produced by rays deflected by the intermittent rectified current, and was several centimetres from the former. No third spot was visible, nor was the undeflected spot even noticeably widened on the side remote from the second spot. With the cutting off of the polarizing current, there was produced a band of fluorescence to each side of the centre spot, the contrast between the two conditions being very remarkable.

It was hoped to apply the device in conjunction with a mercury break-interrupter, but work in this connexion has been postponed for want of leisure. In a preliminary trial of such an arrangement one interesting fact came to our notice. It is probable that a single flame will not act as an efficient rectifier with much higher voltages than those we used, since the flame is strongly acted on by intense electrostatic fields, and cannot be made to vibrate regularly in the spark-gap. Besides, the gap has to be of considerable width, and it seems clear that several flames side by side (all vibrating in synchronism) will be necessary in such cases. There should be no great difficulty in devising an arrangement of this kind.

SUMMARY.

High-tension a.c. current can be rectified by interposing in the circuit one or more spark-gaps, in which the conductivity is altered in synchronism with the e.m.f. by means of a vibrating flame. Apparatus acting on this principle is described, and an account given of some tests of its operation.

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A SENSITIVE VALVE METHOD FOR THE MEASUREMENT OF CAPACITY, WITH SOME IMPORTANT APPLICATIONS.

BY

JOHN J. DOWLING, M.A., F.Inst.P.;

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XVII.

A SENSITIVE VALVE METHOD FOR THE MEASUREMENT OF CAPACITY, WITH SOME IMPORTANT APPLICATIONS.

By JOHN J. DOWLING, M.A., F.Inst.P.

[Read December 21, 1920. Published February 21, 1921.]

I.—*Outline of Principles.*

When alternating potentials of increasing amounts are applied to the grid-circuit of a three-electrode valve, the negative terminal of the filament being connected to the a. c. supply, the plate-current is found to vary, as shown in curve II, fig. 1. This curve, of course, starts from the axis of zero-potential at the point A, where the ordinary characteristic curve for steady grid-potentials crosses this axis (curve I, fig. 1). We will call the curve II the a. c. characteristic of the valve.

If an alternating e.m.f. E be applied to the terminals of a circuit comprising a high resistance R in series with a condenser of small capacity C, there will be a drop of potential v across the terminals of R, given approximately by :—

$$v \doteqdot 2\pi n RCE, \quad . \quad . \quad . \quad . \quad (I.)$$

where n is the alternation frequency.

Suppose this potential v be applied to the grid-circuit of a valve, as shown in fig. 2. A deflection of the milammeter will be obtained which depends on v, but will, in general, be somewhat less than that indicated by the a. c. characteristic for an alternating potential v. There are two reasons for this. Since the resistance R is large—perhaps half a megohm—the valve will be operating with the grid at an average negative potential of a few volts ; in the second place, the resistance of the grid-circuit, being in parallel with R, lessens the effective value of v.

It will be found, however, that the milammeter deflections increase almost linearly for increasing values of the capacity C. The arrangement may consequently be utilized for the measurement of capacity if we construct a calibration curve by observing the milammeter readings due to known values of capacity. In this form, however, the apparatus has a limited range, and is neither very sensitive nor accurate. For zero capacity, or, what comes to the same thing, with no alternating e.m.f. acting, there is

still a considerable current indicated by the milammeter. In order to obtain a sensitive arrangement it is necessary to balance this "zero-current" by an opposite steady current. We may then substitute a sensitive galvanometer for the milammeter, with the result that small capacities can be measured.

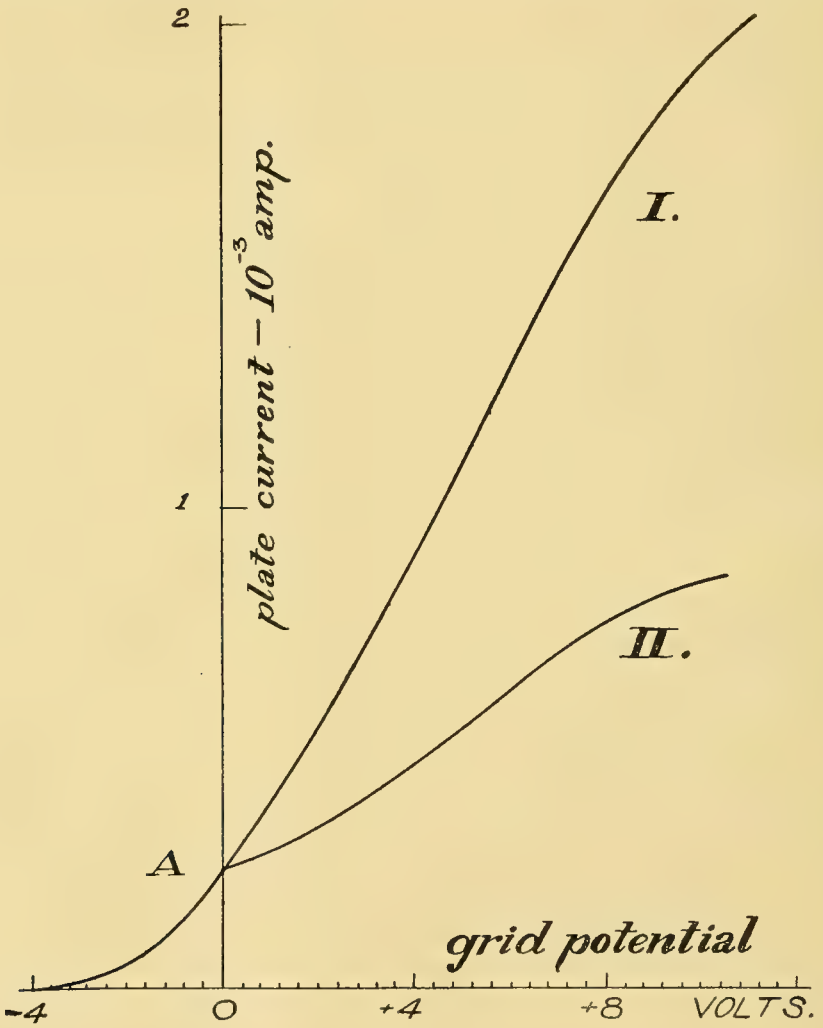

Fig. 1.

By an obvious extension of the same principle, if we balance the greater part of the plate-current, due to a rather large capacity in the grid-potential circuit, it becomes possible to make very accurate comparisons between two condensers of nearly equal capacity, or to study slight variations in the capacity of a given condenser. Such variations may be caused by alteration

of the dielectric between the condenser-plates, or to movements of the latter relative to one another. It is principally in the latter connexion that the device has its widest field of application; and I shall give in this paper a brief account of some preliminary work done in that direction.

I may say, at the outset, that I have not yet tried to push the apparatus, even in its present form, to the highest possible sensitivity, but have aimed rather at determining the sensitiveness obtainable under ordinary working conditions. As is well known, in developing an apparatus of high sensitivity, in proportion to the augmentation in sensitiveness, unsteadiness and variability of the readings become more pronounced. To derive the fullest measure of

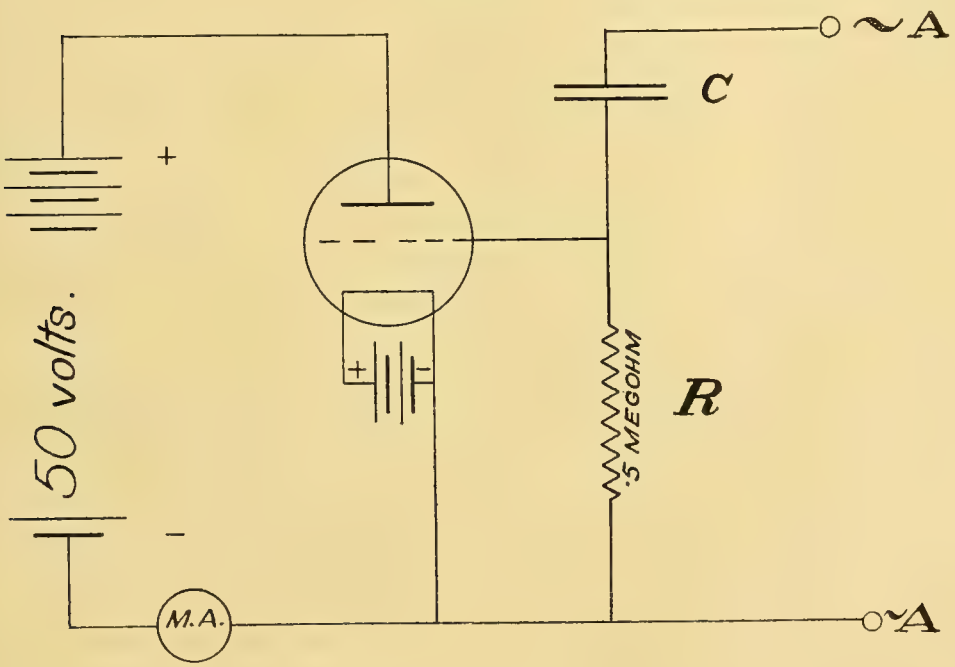

FIG. 2.

performance from such apparatus, a great amount of attention and care has to be devoted to the perfection of its parts, and the elimination of small disturbing influences. Even without such special precautions, the performance of the present apparatus has been remarkably good.

II.—*Experiments with Condensers.*

In the greater number of tests to be described, the valve, an Ediswan E.S. 1. type receiving valve, was operated with 50 volts in the plate-circuit, the filament being heated by a four-volt accumulator, the negative

terminal being connected to the plate and grid-circuits. The curves (fig. 1) represent the characteristics under these conditions.

A few preliminary observations were made in the manner indicated in fig 2; but these were merely made with a view to testing the possibility of the method, and, as this mode of working is very insensitive, it is not necessary to quote any of the results obtained. The first modification tried was to balance the current in the milammeter (fig. 2) by an opposed current from a single cell in series with an adjustable high resistance. Some experiments were made thus, a Paul Unipivot galvanometer with an

Fig. 3.

universal shunt being employed in place of the milammeter. As it was convenient to utilize the laboratory supply for the 50-volt plate-circuit battery, it was found impossible to connect the town supply of 200 volts a.c. directly to *AA* in consequence of the insufficient insulation between the a.c. and d.c. circuits. An insulated 200-volt a.c. supply was therefore obtained, using a small step-up transformer from the 12-volt a.c. galvanometer lamp circuit. Beyond this no special care was taken as regards insulation or shielding of the apparatus. A few observations were thus made, using a graduated air-condenser of the rotating-sector type. This

graduated from 100 to 1,200 micro-microfarads, and in one experiment R was made 200,000 ohms. The relation between the galvanometer deflection and capacity was almost linear, as shown in the curve (fig. 3), the condenser graduations being unreliable for the smaller values.

A very sensitive moving-coil galvanometer[1] was then substituted for the Unipivot instrument, the universal shunt being retained, and the connexions altered to those shown in fig. 4. This had the advantage of being more compact, as only one storage battery was required. Preliminary observations were made, as before, with the graduated air-condenser, and the expected high sensitivity of the apparatus was fully obtained. For example, with a

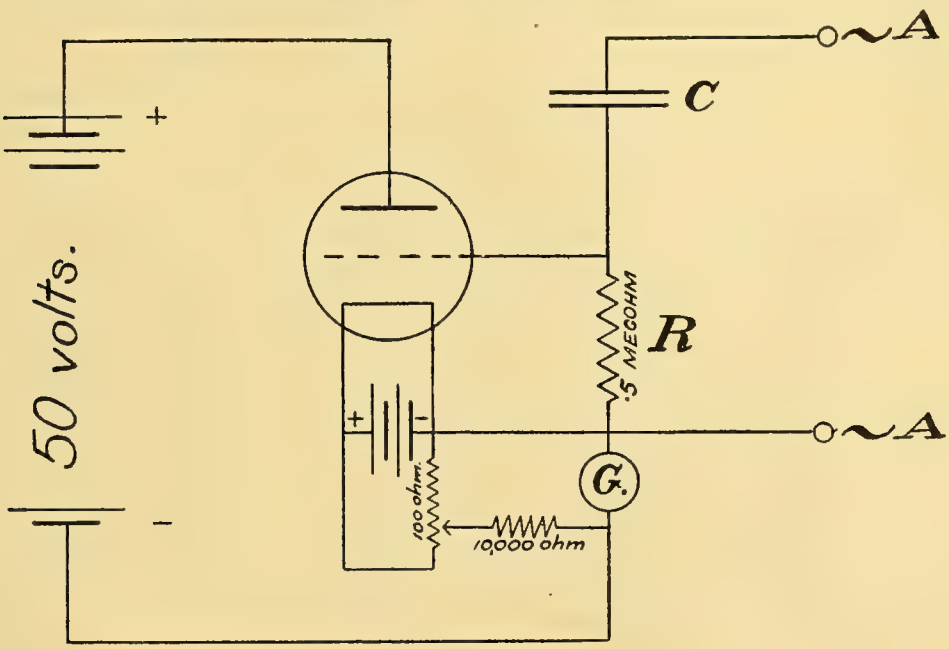

FIG. 4.

capacity of 100 micro-microfarads (10^{-10} farad) an alteration of 1 per cent. in the capacity produced a deflection of 300 scale-divisions, the galvanometer shunt being at 10.[2] With this degree of sensitiveness the deflections were fairly steady, but, with a lower value of the shunt, the spot of light commenced to execute irregular movements, rendering accurate readings impossible.

---

[1] Elliott's "Century" galvanometer: 1,000-ohm coil; $2{\cdot}5 \times 10^{-10}$ amp. per scale-division.

[2] In view of the fact that the resistance of the plate-circuit is very high, and that the galvanometer and shunt were in circuit with 10,000 ohms in the potentiometer-circuit, the actual shunt values were not very different from those marked on the shunt itself.

This unsteadiness was principally due to fluctuations in the a.c. supply, but also partly to the fact that the apparatus was insufficiently shielded and imperfectly insulated. A large sheet-metal box was procured, and the valve, resistances, condenser, and filament-battery were placed on sheets of ebonite within. The connexions to the a.c. and d.c. supplies and to the galvanometer were, of necessity, still exposed; but, nevertheless, a considerable improvement in the steadiness of the readings was found. It appeared likely that the

Fig. 5.

remaining unsteadiness was chiefly due to the a.c. fluctuations. It must be remembered that, when the greater part of the plate-current is balanced with the potentiometer, the current through the galvanometer is a *difference effect*. Just as a small change in the capacity C produces a large effect on the galvanometer, so will small variations in any of the other quantities which occur in equation (I).

III.—*Application of foregoing as an ultra-micrometer and micro-pressure gauge.*

The first trials were made with a simple form of plate-condenser, in which one of the plates was movable normally by means of a micrometer-screw. The two plates were 2·5 cms. in diameter, and were carefully ground to a plane surface. The movable plate was attached to the end of a short rod, which was ground to a smooth sliding fit in a short length of brass tube. This tube was screwed in in place of the anvil of a micrometer-screw gauge, and a couple of springs were arranged to pull the sliding-rod so that its extremity made tight contact with the end of the micrometer-screw. This arrangement was screwed to the long leg of an L-shaped piece of ebonite, so that the other plate, supported on a rod inserted in the shorter limb of the L, was opposite the first plate. By a device which I shall describe later, the two plates were made exactly parallel, and the micrometer allowed them to be moved apart any desired fraction of a millimetre.

An example of the results obtained with this rough arrangement is given in fig. 5, where the abscissae give the micrometer readings in thousandths of a centimetre. The points lie nearly on a straight line over the range covered; but the sensitiveness is not very great. The fact that the points lie a little to one side or the other of the line is obviously due to the imperfect action of the screw.

It is easy to see that the sensitiveness can be greatly increased by bringing the plates closer together, and also by enlarging the areas of the plates. With plates close together and of moderate size, they form a condenser of which the capacity is much greater than that of the grid and other connexions. In equation (I) we can thus regard C as wholly the capacity of this condenser. C will then be given by the formula—

$$C = \frac{A}{4\pi t} \div (9 \times 10^{11}) \text{ farads.}$$

And we may write (I) in the form—

$$v = B \cdot \frac{A}{t} \quad . \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

if we include all the other quantities in the constant B. Now, the slope of the a.c. characteristic being practically uniform, a given *change* in v will produce a corresponding change of constant amount in the galvanometer reading, no matter what may be the actual value of v. Consequently, the condition for sensitiveness is that $\frac{dv}{dt}$ should be as great as possible. But

$$\frac{dv}{dt} = - B\frac{A}{t^2}, \quad . \quad . \quad . \quad . \quad \text{(III.)}$$

hence the sensitiveness increases directly in proportion to the square of the linear dimensions of the plates and inversely as the square of their distance apart. The negative sign, of course, indicates that as the plates are moved apart the grid potential v diminishes.

In the next apparatus set up, two circular metal plates 7 cms. in diameter were utilized. One of these was cemented to the table of a Leitz microscope. The fine adjustment-screw of this had a large divided head, each division of

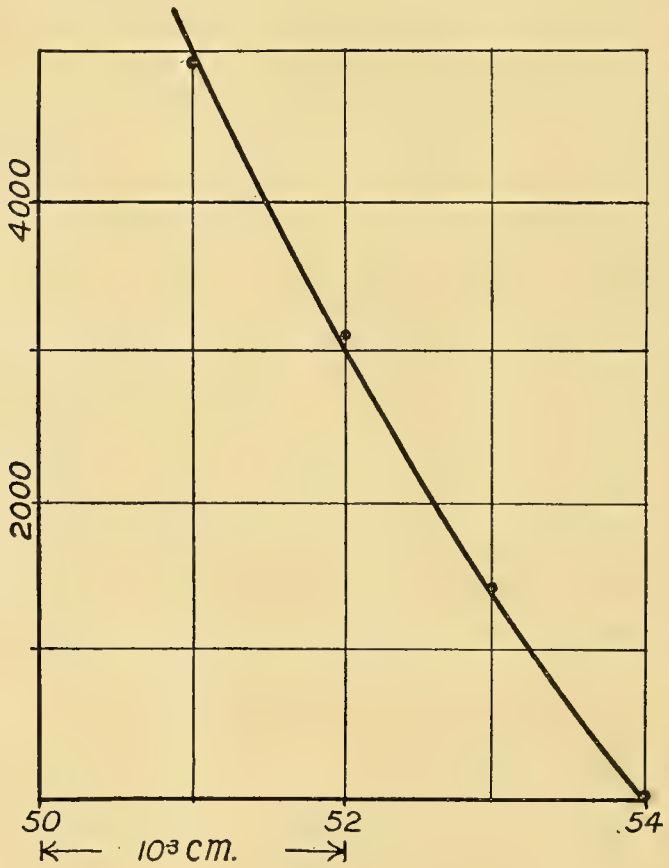

Fig. 6.

which corresponded to a vertical movement of the microscope tube through $\frac{1}{2000}$ cm., and $\frac{1}{5}$ of a division was easily readable. The strong spring of the fine adjustment effectually prevented backlash. A strong glass tube was supported in the microscope tube by two stout plugs which held it very rigidly, and the lower extremity of this tube was introduced into a small metal cup attached to the centre of the upper condenser-plate. While this plate rested on its

fellow, the cup was filled with molten fusible metal (90° C. m.p.), which rapidly cooled and cemented the metal plate to the glass support. When cool the plates were separated by turning the micrometer screw the desired amount. This condenser allowed a much higher sensitivity to be attained. Fig. 6 shows the first set of observations thus obtained. During this set the apparatus was shielded in the metal box previously mentioned, and the conditions were fairly steady. The points lie almost on a straight line, but the gradual increase in sensitiveness with decreasing separation of the plates is just noticeable, the points really lying on a parabolic curve. (The observations were taken with the galvanometer-shunt at 10, but the ordinates in fig. 6 have been plotted as if the galvanometer was unshunted.) The average sensitivity throughout the range is about 3200 scale divisions for $\frac{1}{1000}$ cm.; i.e. 1 division deflection corresponds to a displacement of about 3×10^{-7} cms.

Several sets of observations were made with this apparatus with the plates at different distances apart; and it seemed probable that, under sufficiently steady conditions, it would be possible to detect a displacement of at least $\cdot 5 \times 10^{-7}$ cms. Further work with the apparatus is still being carried on, and I will not, therefore, give further particulars in this paper.

A sensitive pressure-gauge may easily be constructed involving the same principle. A shallow recess was turned in an ebonite disc, and a flat metal disc (6·4 cm. diameter) was cemented therein, so that its surface lay about 2 mm. below the ebonite rim. A similar disc, about ·6 mm. in thickness, was cemented to a sheet of india-rubber (such as is used for foot-bellows). The rubber was then cemented to the ebonite rim while slightly stretched, the metal plates being thus supported about 1·3 mm. apart. Suitable connexions were, of course, made by fine wires from each of these plates, and a tube through the ebonite gave connexion with the air-space inside. When the pressure rises within, the plates are driven apart, and the capacity of the system diminishes. The apparatus was roughly tested, and it was found that a pressure excess of 1 cm. of water resulted in a deflection of the galvanometer (shunt = 10) of about 300 divisions—or, roughly, 3 galvanometer divisions (unshunted) corresponded to a pressure of 1 dyne per cm.^{2} It is obvious that with improved construction, larger discs both of metal and rubber, thinner rubber, and closer proximity of the plates, it should be possible to measure very minute pressure differences indeed.

I have said enough to indicate the possibilities of the method, and hope to publish further particulars when I have succeeded in attaining satisfactory

steadiness in its operation. So far as the present observations go, the degree of sensitiveness falls a little short of that obtained by Whiddington[1] for his ultra-micrometer. However, the advantages of using a deflection method would in many cases compensate for a slight lack of sensitivity. I shall, however, reserve for a future occasion a discussion of this point, and of some other considerations relative to the practical employment of the method.

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[1] Whiddington, Phil. Mag., vol. xl, Nov., 1920, pp. 634-639.

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A DIRECT READING ULTRA-MICROMETER.

BY

JOHN J. DOWLING, M.A., M.R.I.A., F.Inst.P.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XVIII.

A DIRECT READING ULTRA-MICROMETER.

By JOHN J. DOWLING, M.A., M.R.I.A., F.Inst.P.

Read January 25. Published March 4, 1921.

In a recent communication[1] to the Royal Dublin Society I described an electric valve method for the measurement of capacity, which could also be applied to the measurement of extremely small displacements; but, inasmuch as a very constant source of alternating e. m. f. was necessary for its operation, further work was promised with a view to overcoming this drawback. In the course of this work, the present method suggested itself, and, on trial, was found to be even more sensitive than that previously described. It has the great advantage of simplicity, and, although capable of extraordinary sensitiveness, is singularly free from that unsteadiness to be expected in a highly sensitive apparatus. Furthermore, with a suitable adjustment of the apparatus, it is possible to maintain a high and almost constant degree of sensitiveness over a total displacement of, perhaps, one-tenth of a millimetre.

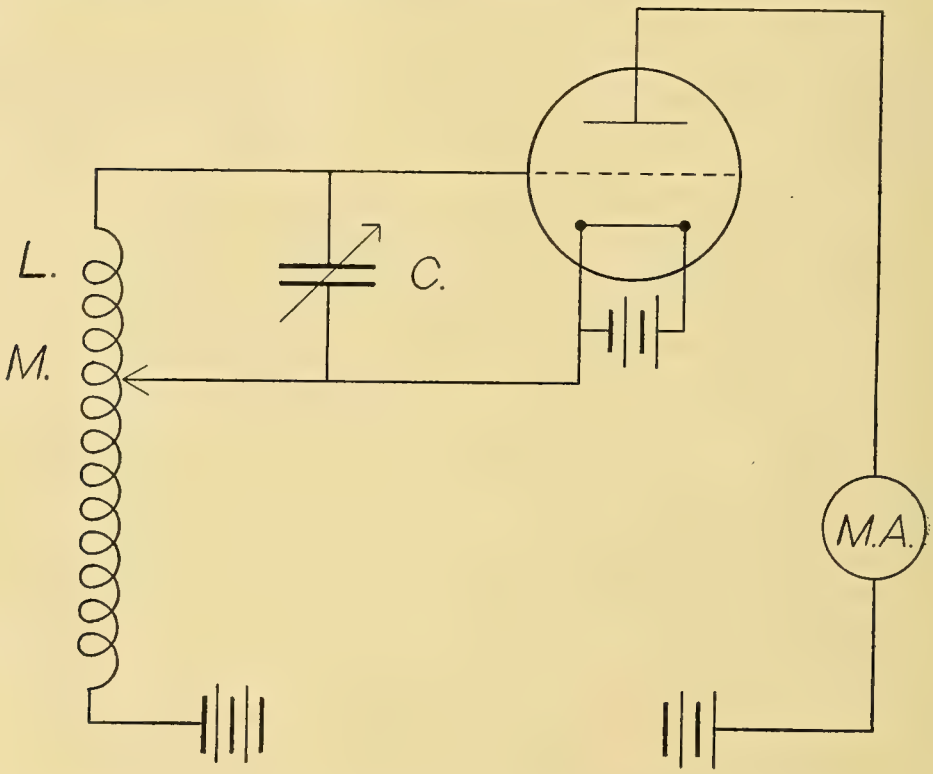
In the present communication I shall confine myself to a short description of the apparatus in the form first set up, together with an account of some trial measurements made with it. I shall reserve for another occasion a fuller consideration of the principles involved, and of the conditions of operation of the device.

It is well known that for sustained oscillations to occur in a three-electrode valve circuit, the values of the inductances and capacity must fall within certain limits. If the self-induction and the coupling of the valve circuit shown in the figure be left unaltered, while the capacity is gradually changed, two effects are produced: the frequency of the oscillations changes and their amplitude is also, in general, affected. The former phenomenon was that availed of by Whiddington in the construction of an ultra-micrometric device.[2] The latter may be regarded as the effect upon which the present device depends. As the amplitude of the oscillations of potential varies, a corresponding change takes place in the plate current, and it is this property of the oscillating circuit which is utilized.

[1] "A Sensitive Valve Method of Measurement of Capacity." Scient. Proc. Roy. Dub. Soc., vol. xvi, No. 17, p. 175. 1921.

[2] Phil. Mag., Nov., 1920, vol. xl, pp. 634–639.

The connexions of the oscillating circuit shown in the figure were slightly modified in practice, a potential balancing device, similar to that described in my previous paper,[1] being employed so as to permit a sensitive galvanometer to be substituted for the milammeter *A*. An ordinary B.T.H. receiving valve was employed, and a negative potential of a few volts was found necessary in the grid circuit to obtain good oscillatory conditions. In the preliminary experiments a coil of about 10^6 cms. inductance was used,



the portion *L* being usually about one-quarter of the whole. An air condenser, having a range of 100 to 1,200 micro-microfarads was used in the course of these preliminary tests. I may mention that the currents in the plate circuit varied from one-half to several milliamperes, and that it was convenient to employ an Ayrton-Mather universal shunt with the galvanometer to facilitate preliminary adjustments.

One consideration is of importance in the working of the apparatus. With a given adjustment of the inductances, it is found that there is a

[1] *loc. cit.*

certain value of the capacity, sometimes more than one, for which the plate current reaches a maximum. It is clearly necessary to adjust the apparatus so that it is not functioning near such maximal points.

The first trial of the apparatus as a micrometric device was carried out as follows:—Two circular plates of steel, 6·4 cm. in diameter, and ground reasonably flat, were mounted on the stand of a Leitz microscope. One was cemented to the platform, while the other was carried on the end of a glass rod which projected from the microscope tube, in which it was firmly supported. The two plates were adjusted to be exactly parallel. The fine adjustment screw of the microscope was furnished with a divided head, each division of which corresponded to a vertical motion of the tube through $\frac{1}{200}$ mm. It was thus found possible to move the upper plate through this distance with reasonable certainty, the screw adjustment being remarkably good.

Observations were made as follows:—The galvanometer being shunted, the plates were screwed apart a certain number of divisions, and the sliding resistance S adjusted until the galvanometer was at zero. The shunt was then gradually reduced; slight further adjustments of S being made, if necessary, while this was being done. Except in the most sensitive settings, the shunt was reduced to unity, and observations then made of the deflection of the galvanometer resulting from the rotation of the microscope screw through one scale division. It was generally found that a deflection of at least two or three hundred divisions was thus produced; but, by selecting a suitable initial separation of the plates, much larger deflections could be obtained. It was easy to set the apparatus so that about six hundred galvanometer divisions corresponded to one division of the screw; that is to say, a displacement of $\frac{1}{2000}$ cm. produced a deflection of the galvanometer of six hundred scale divisions. In other words, a displacement of $\frac{1}{1,200,000}$ cm. was detectable unmistakably. On more than one occasion a much higher sensitivity was reached, but its magnitude could not be stated with certainty. The smallest movement that could be given with any certainty to the plates was that represented by one division on the screw-head. The highest sensitivity that could be utilized was, therefore, already reached when the galvanometer deflection extended, as just mentioned, six hundred divisions from one end of the scale to the other. By shunting the galvanometer, the effect of moving the plate could be reduced, and an estimate formed of higher degrees of sensitivity. However, I am not at present certain if the sensitivity thus estimated is correctly given by multiplying the galvanometer reading by the shunt ratio.

In order to produce displacements of sufficiently minute nature, another

plan was adopted. A brass rod, having a diameter of one-eighth inch, was suspended vertically in a wooden frame. Two circular brass plates, 10 cms. in diameter, with three-sixteenth inch holes drilled at their centres, were carefully ground to a plane surface and cemented to ebonite blocks, which were drilled to slide smoothly on the rod. The two discs were then fixed in position, so as to be separated by ·12 mm., and to be as nearly parallel as possible. The ebonite blocks were each furnished with a set-screw, and it was assumed that if the rod were subjected to tension the plates would then be moved apart by the amount that that portion of the rod between the two set-screws increased in length. The screws were approximately 1·5 cms. apart on the rod.

With this apparatus it was found that the highest sensitiveness obtainable with this ultra-micrometer was even greater than had been suspected. For one particular adjustment of the inductances the galvanometer was quite stable in the absence of accidental vibrations, but nevertheless an extraordinary degree of sensitivity was displayed. Thus, it was found that a deflection of four hundred and ten divisions of the galvanometer was produced when a load of five hundred grammes was suspended from the rod. A simple calculation shows that such a load applied to a brass rod one-eighth inch diameter will produce an extension of $9{\cdot}6 \times 10^{-6}$ cm. in a length of 1·5 cms., assuming Young's modulus for brass to be 10^{12} dynes per sq. cm. As this extension corresponds to four hundred and ten divisions of the galvanometer, we may, in round numbers, say that a displacement of $10 \times 10^{-6} \div 400$, or $2{\cdot}5 \times 10^{-8}$ cm. was detectable. With a more sensitive galvanometer perhaps a further limit might have been attainable, but in view of the possible unsteadiness of the readings one cannot predict what the lowest attainable limit might be. The number quoted was obtained under very unfavourable conditions, no screening of any kind being placed around the apparatus, and the only precaution taken by the operator being to stand as still as possible while lifting and lowering the weight by a string. A movement of the hand towards where the apparatus lay on the table was sufficient to cause a perturbation of the galvanometer. I have no doubt, however, that by enclosing the apparatus as far as possible in a metal box, as is the usual practice with oscillatory circuits, this trouble will be eliminated.[1]

A careful series of tests with improved apparatus is now being undertaken, the results of which I hope to embody in another communication.

[1] This trouble has since been completely overcome.

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STUDIES IN THE PHYSIOGRAPHY AND GLACIAL GEOLOGY OF SOUTHERN PATAGONIA.

BY

E. G. FENTON.

[COMMUNICATED BY PROFESSOR G. A. J. COLE, F.R.S.]

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(PLATES V, VI, and VII.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XIX.

STUDIES IN THE PHYSIOGRAPHY AND GLACIAL GEOLOGY OF SOUTHERN PATAGONIA.

By E. G. FENTON.

(COMMUNICATED BY PROFESSOR G. A. J. COLE, F.R.S.)

[Read January 22, 1918. Published March 16, 1921.]

I.

General Features of the Region.

In the present paper I propose to deal with the quaternary and recent geological history of a certain limited portion of Patagonia in which I lived for a period of seven and a half years. The appointment which I held during that time gave me abundant opportunities of visiting the "Camp" generally and studying the superficial features of the country. I was unfortunately never able to visit the country north of the Santa Cruz river to any great extent, or south of the Straits of Magellan; nor did I ever succeed in getting as far as the chain of the Andes or those most interesting channels or fiords which penetrate the southern cordilleras of Patagonia. However, I found in the eastern plains, even limiting myself to a small portion of their recent history, abundant materials for study.

This district, lying between the Santa Cruz river and the Straits of Magellan in the one direction, and extending from the Andes to the Atlantic in the other, consists chiefly of plain or pampa, its level varying from four to five hundred feet along its eastern edge up to perhaps eight hundred or even in places a thousand feet further west.

If we begin our study by taking a typical portion of the high pampa on the north side of the Gallegos river, the first thing that will strike us (Pl. VI, fig. 1) is its extreme flatness of surface. This extraordinary flatness is characteristic of all the eastern plains of Patagonia north of the Gallegos river; and when travelling through the country the landscape becomes at times almost terrible in its monotony; not even a single hillock can be seen to break the everlasting evenness of the horizon.

After travelling a certain distance, however, over the plain, the monotonous scene depicted above may change without warning. Suddenly a huge valley may be found to lie below us, hundreds of feet deep, extending for miles, and eventually rising once more in the distance to the original level.

Along the bottom of this valley, which will be found to run from west to east, a small and, comparatively speaking, insignificant river will in most cases be observed, flowing sluggishly in various sinuous curves, and small, out of all proportion, to the size of the valley in which it is found. These river valleys begin, as a rule, among the hills to the west, and extend to the Atlantic; but besides these, we occasionally come across other valleys which are found, after being followed for some miles, to begin blindly, and end in the same manner; in fact, they are hollow, cup-shaped, or, more correctly speaking, dish-shaped, depressions scooped out of the pampa, and have in their lowest parts, instead of a river, as a rule, one or more salt lagoons. These are the "bajos" of Patagonia, and are some of the most puzzling features found in the district. There are also numbers of long, more or less narrow valleys styled "cañadones," running as tributaries to the river-valleys and bajos. These vary in size, and often cut deeply back both to the north and south into the pampas. Sometimes they run for many miles, and although, as a rule, they are dry, at times a small stream runs down the centre.

In this eastern portion of Patagonia no trees are ever found either on the pampas, valleys, or cañadones, but the surface of the ground is everywhere clothed with a coarse grass, and in places with a scrubby bush a foot or two in height. The condition is one found generally in steppe countries.

The descent from the higher valleys to the river level below is not in the form of an inclined plane, but in a series of steps or terraces. These latter vary in number in different localities; in some places there are seven, in others only one or two, whereas in others we may find the pampa falling direct in one drop to the river below.

Besides this condition of extreme flatness which I have mentioned, we shall also see, if we examine fig. 1 carefully, that there is evidence of considerable erosion having taken place in the surface of the country as well as the levelling action.

In the foreground of fig. 1 we are looking across a large cañadon which has eaten back into the country from the Atlantic. Now, if we come down on to one of the terraces we may possibly see a peculiar flat-topped hill standing out in a very bold manner some considerable distance, perhaps a mile or so from the edge of the pampa. The level of the top of one of these hills is found to be the same as the general plane of the pampa; in fact, the hill is an isolated portion of the pampa which has been able to resist the great

erosive action that cut out the river-valleys and cañadones. In one place the top of one of these hills was found to be 520 feet above the river, and this was the same as the level of the nearest high pampa.

The next question in the study of the pampa is the shingle, which, as C. Darwin and others long ago pointed out, is found practically all over the plains of Southern Patagonia. In fact, I do not believe there is a single square yard of the high pampa between the Straits of Magellan and the Santa Cruz river without its shingle covering. The shingle forms a comparatively thin layer, varying from 10 to 25 feet in thickness. It lies in practically every instance on well-stratified middle tertiary rock, the latter in most cases consisting of a more or less whitish, greyish, or dull blue soft stone, locally called Tosca. This peculiar formation, although apparently sedimentary, has yielded nothing but mammalian and bird fossils. The pebbles on the surface are as a rule broken and angular, as the result of repeated pampa fires; but below the surface they are comparatively well rounded and sufficiently worn to show that they have been subjected to prolonged water action.

The diversity in composition of the individual stones which make up this shingle is remarkable. Some are white, some are black, some are yellow, some are red, and some are green; but by far the greater number in most localities consists of a yellowish porphyritic variety. No particular bedding, either false or true, is to be seen in any of these layers of shingle; in fact, they give one the idea of ballast dumped higgledy-piggledy out of wagons to fill up the place. This same absence of arrangement of the stones is to be found in almost all parts of the first pampa. The stones found on the pampa are often as much as six to eight inches in length, and we might call the greater number of them three-quarters rounded, many of the stones still exhibiting the original sides, and having only the corners smoothed off.

I would once more wish to impress on the reader that one of the most extraordinary characteristics of this shingle is its universal and even distribution; it is spread broadcast, practically without a break, over almost the whole surface of Argentine Patagonia. It is found on the highest hills, in the lowest valleys, and even extends, as has been shown by the Beagle expedition, for hundreds of miles into the Atlantic under the sea. It never occurs in heaps, and, as seen in the cliff sections, the underlying rock shows, when completely covered by this shingle, practically no indentation or cuttings—in fact, it exhibits the same wonderful levelness that the overhanging shingle does. The unconformity between the two is apparently very slight, and yet there must have been a very considerable hiatus in time between the depositions of the two formations.

As we trace the face of a cliff down on the Atlantic coast, there is no

repetition of the shingle-layer; practically all the rock is what I have described as Tosca. It is well stratified, showing very even bedding; in some places, however, one can see layers cropping out up to several feet in thickness, composed chiefly of marine shells. Where shingle occurs down the face of a cliff it always seems to mark the remains of old river-beds. The pebbles found are of a very different composition from those found on the pampa the layers are limited in extent laterally, and they never run along the cliff more than a few hundred yards in one place. There is, as a rule, distinct and well-marked unconformity between this latter shingle and the surrounding rock; and, when we consider that these tertiary river-beds are very rare and only found in a few places, we realize that there is practically no resemblance between them and the great layer of shingle found on the pampa.

From these facts we can conclude that this layer of pampa shingle is a unique formation, and that there is no parallel to be found in this country—at least in the earlier rocks. Now, if this shingle-layer was a beach or marine formation, as Darwin tried to prove, we should surely have found in the rocks beneath some repetition of it formed when the country began to subside under the sea or to emerge from it. Especially should this be the case when we consider that these subsidences during tertiary time extended right to the cordillera, as is proved by similar marine formation being found well among the mountains. Consequently, I think the marine theory must be abandoned. The next point of importance with regard to this shingle-layer is that in all the localities where I have examined it between the Santa Cruz river and the Straits of Magellan I have found it unfossiliferous. I understand that to the north of San Julian and Deseado in many places recent sea-shells are found on the surface of this layer; but from what I have gathered from intelligent people who have visited the locality in question, these shells are not found to any depth in the shingle. This would indicate that they represent a recent subsidence long after the shingle had been spread out over the country. I have myself noticed on many occasions mussel shells lying in heaps, mixed with the excreta of sea birds, on the pampa upwards of two miles or more from the beach, so that we should always bear in mind the possibility of carriage by birds when considering isolated instances.

II.

Relations between the shingle and the surface on which it was laid down.

If we go round the point at the mouth of the Gallegos river and turn to the north along the Atlantic coast, when we get as far as the first pampa level we see, as we have said, all along the top a darkish-brown layer, lying

apparently conformably on typical tertiary rock. On examining this rock, however, it is found not to consist of pure shingle, as one would imagine from having seen the similar formation in other places, but to have a composite structure. The shingle is found above as elsewhere, but below this there is another layer of equal thickness of marine formation holding an abundance of fossilized sea-shells. This marine layer has been described by Mr. J. B. Hatcher, and named by him the Cape Fairweather Bed. The unconformity between the Cape Fairweather Bed and the tertiary rock is slight but distinct, whereas there seems to be in places none between the Cape Fairweather Bed and the shingle, the two layers passing imperceptibly into one another. In no instance in the district in question have I yet found any formation overlying this shingle except lava; the latter exists, however, in extensive sheets in many localities, and will be dealt with in a later section.

We have already seen that the apparent unconformity between the shingle and the tertiary rock is on the highest level always insignificant; it will consequently be evident that, even if all the shingle were removed, the pampa would still possess that extraordinary flatness which I have mentioned as existing everywhere, and it will be further evident, moreover, that this flatness must have been a primeval condition, and must have existed before the shingle appeared. It would seem also that the shingle crept down gently and gradually over this smoothed and level pampa until it completely covered it, and that the transition from the condition of the climate which brought about the planing off of the pampa to those which covered the latter with sand and shingle was completely devoid of violence. The tertiary rock underlying the Cape Fairweather Bed has been generally looked upon as belonging to the Miocene system; this would place the Cape Fairweather Bed either in the late Miocene, the Pliocene, or early Pleistocene. The unconformity between the Cape Fairweather Bed and the tertiary rock is, as we have seen, slight; but it does not follow necessarily from this that there was a short hiatus in time between the periods when they were respectively deposited. It may only mean that the great planing off process extended much further back into tertiary times than we might have thought, and was operating before the Cape Fairweather Bed was formed. We have evidence from other sources that the tertiary rock suffered considerable erosion before the shingle came down, and that it once extended to a much greater altitude; it would consequently seem that the elevation and subsidence which occurred during tertiary times took place very gradually. This is particularly clear when we remember the complete absence of faulting and folding found in these rocks, and the perfect horizontality of the strata composing them. All these facts would point to a condition of affairs in pre-

shingle times as that of a dry, probably warm, climate, with high winds; in other words, an exaggeration of the climatic conditions which prevail at present, with less snow and greater warmth. At present the summers of Patagonia are very dry, and high westerly winds prevail; great quantities of dust are blown every year from the pampas into the Atlantic; still very little impression is made on the general outline of the country, as the surface is everywhere protected, not only by a coarse grass and bush, but by twenty odd feet of shingle which is spread over it. It is only near the settlements, where the grass and scrub become eaten down and trampled away, that the winds may be seen to make any impression, and it is from such places, and from the roads which are now everywhere being made in the country, that the chief part of the dust is derived. I am informed that a few years ago, before this became a sheep-farming country, the grass was everywhere much longer than it is at present, and consequently the protection to the surface was greater. In the springs of the years, when the snow is melting, a certain amount of erosion also takes place from the floods, but this only occurs in the cañadones and valleys, and even here very little cutting is found to have taken place, except in those cañadones where the surface has been broken by wheel-tracks or other traffic. For instance, the winter of 1913 was a very severe one, and there was much snow and rain, the floods in the spring being enormous, and yet, on carefully examining quite a number of cañadones where there was no traffic, I was surprised to find that there was practically no erosion of the surface, except a few tiny gullies, six inches wide and deep, which would be obliterated with one month's dust and growth of vegetation. Such winters occur only once in ten years as a rule, and hence the present climatic conditions are incapable of producing the surface state of Patagonia as we now find it. If, however, the shingle were removed, and the climate slightly altered, so that the winters were more dry, and the winds in the summer perhaps a little stronger, we should have all the conditions necessary to produce that great flat country which must have existed in Patagonia in pre-shingle days.

It appears that after a long period of dry, windy climate, probably in late tertiary times, the conditions began to alter, and that slowly, gradually, and without violence the shingle began to creep down over the pampas until it reached the Atlantic. No carving or cutting of the country took place during this period, which probably lasted for a long time; in fact, at the end of the great shingle period the country was probably as flat and even as before. None of the great river valleys, in my opinion, existed then, and there were probably no bajos.

As we have seen, the Cape Fairweather Bed is a marine formation,

which lies with slight unconformity on the tertiary rock, and is in turn overlain by the shingle; this arrangement, however, is not as simple as would at first sight appear, and on careful examination one will find that there is a more or less distinct transition layer between the Cape Fairweather Bed and the shingle. In a typical locality, such as is seen in Cape Fairweather proper, we have first of all lying on the tertiary rock a layer of fifteen feet, consisting almost exclusively of oyster shells imbedded in a fine sandy matrix; over this layer is another in which there are many different varieties of sea-shells as well as oyster-shells; the latter, in fact, are in a minority; but in addition to shells—and this is of the greatest importance—there are to be found a fair number of typical pampa pebbles. This layer varies from two to three up to ten or fifteen feet in thickness, and the various shells, pebbles, etc., are held together by a hard rusty-brown material; in some places there is well-marked true bedding, with thin laminae of a hard stone; in others there is false bedding, as if of an old beach, while in others there seems to be a more or less homogeneous matrix holding the pebbles and shells together. The layer in which the pebbles assume a false bedded appearance, as if of an old beach, always comes between the shell-layer and the shingle, and tends to fade imperceptibly into both. Now this whole bed would give one the impression of being a shallow-water formation, and the fact that most of the shells are practically complete, with often both valves of the lamellibranchs in position, would show that it has suffered very little disturbance since it was laid down, and would indicate, at the time of its formation, calm shallow water.

These facts are very significant, and tend to show that the transition from the pre-shingle to the shingle periods was gradual; in fact, when the first shingle began to be washed down from the mountains over the plains to the Atlantic coast the climatic conditions were such that these marine molluscs flourished in abundance; also it is clear that calm weather prevailed, and that the floods which carried down the shingle were very mild, and had very little tearing up or grinding action, otherwise the shells mixed with the pebbles would have been all smashed up and ground to powder.

Later on the shingle came down in greater quantities and with greater force, so that in the end the shell-layer became completely covered, and nothing but pure pebbles and sand remained on the surface. These facts also show that at the beginning of the shingle period the level of the main pampa was much lower than at present, and that Cape Fairweather, which is now almost five hundred feet high, was then slightly below or at the sea-level.

III.

Indications that the Shingle was deposited during the Quaternary Ice Age.

With regard to fixing the date of the first great shingle period, the facts that we have to go by are that the layer in question is found superficial to practically all the rocks of the district. The only rock overlying it is the lava, which is found over fairly large areas in many places; also it is unfossiliferous, and is unique, inasmuch as no parallel is found to it in any of the older formations. The higgledy-piggledy arrangement also gives one the idea of its having been carried down by a large volume of slowly running water. The large lava outpourings of this locality occurred during a long period, and were thrown out in great part subsequently to the beginning of the ice age; so that, considering also the similarity of this shingle layer to many of the fluvio-glacial deposits found in the northern hemisphere, we are justified in concluding that the great Patagonia pampa shingle layer belongs to the earliest portion of the Ice Age. The south of the Gallegos river is low and undulatory, and does not seem to belong to the same horizon as the north, and there are many points of difference between the pampas in both localities. On the north, as we have seen, the pampa rises suddenly, or in a series of well-marked terraces, to about five hundred feet, and then extends away indefinitely in the form of a remarkably flat table-land, whereas on the south the plains begin only a few feet above the sea-level, and rise slowly and gradually. At first there are no apparent terraces on the south side, but a little up the Gallegos Rio Chico a terrace appears which would seem, on being traced, to correspond to the lowest terrace along the Gallegos river, and a little further still a second terrace is in many instances found. On the south bank of the Gallegos river, however, about thirty miles from its mouth, one meets once more the typical high or first pampa level, extending down in a V-shaped manner between the Gallegos river and the Rio Chico, or, more correctly speaking, in a long narrow strip a few leagues wide running down along and parallel to the former river, and separated from it by a broad terrace, about two miles wide, and the low flat of the river valley.

On carefully examining this strip, one can see that it possesses all the characteristics of the pampa, such as extreme levelness of the summit, and, where eaten into, flat-topped hills. Already we have seen that at the time when the shingle began to come down, the level of the main pampas was five hundred feet lower than it is at the present day. At that time all the land to the south of this pampa line would be under water, and consequently would not be subjected to the great planing down action of the wind; this

would account for its undulatory surface, and, as we shall see later, its lack of terraces. Nevertheless, although the levels differ to the north and south of this line, the superficial formations would seem to be the same, namely, typical shingle overlying tertiary rock.

Now, when we leave the Rio Chico, and travel southward towards the Straits of Magellan, after a few miles we notice a new feature in addition to the shingle beginning to appear; this is an occasional great erratic boulder.[1] At first such boulders are few, but after a league or two they become more numerous. Some of these erratics are found on the surface, some are half way out, whereas some are practically buried, with only their heads showing. Now, these erratics have the same compositions as the pebbles in the shingle; even amongst the lava sheets, practically none of them consist of lava, and there is a complete gradation in size from the smallest pebble up to the largest block; consequently, one is led to believe that they are part and parcel of the same formation as the shingle, and have come from the same locality. The erratics extend right to the Atlantic coast, ten miles south of the mouth of the Gallegos river, and, like the shingle, they are found equally well marked on the highest hills and in the lowest valleys. A line drawn through southern Patagonia on the Argentine side from a point on the Atlantic coast, about twelve miles north of the fifty-second parallel of latitude due west, to a point about twelve miles to the eastward of the seventy-first west meridian, and then curving slowly to the north, following finally up along and parallel to the cordilleras, would more or less mark the limit of the large erratic boulders. This line is not quite straight, and there are minor curves in it, which, however, are of no great extent. I have traced it as well as I can on the map.

On going further to the north, along the chain of the Andes, one finds erratics extending a certain distance into the plains, but not to anything like the same distance as in the region which I have indicated; in fact, this very abrupt extension outwards towards the Atlantic of the large erratic boulders to the south of the Gallegos river is a very remarkable fact, especially when we consider that the mountains to the west of this district are insignificant as regards height in comparison with those to the north and south.

Now, although the pampas to the south of the Gallegos river, near its mouth, belong to a lower level than those to the north, yet further to the west they both merge with one another, so that at a point sixty miles from the coast all the pampas, both north and south, are on the same level; here

[1] Compare B. Hatcher, American Journal of Science, ser. 4, vol. iv, p. 348, 1897.

the great erratics lie in and on the shingle belonging to the first pampa level. All the shingle extending from the south and west towards the north and east over the high pampas is one continuous layer, and belongs to the same formation, and may be divided by the line I have indicated into two divisions, a shingle area and a shingle erratic area. This evidence will confirm the view already put forward that the shingle layer belongs to the Ice Age. I have, moreover, carefully examined the erratic boulder area, and found abundance of scratched stones in it, like those found in the boulder clay of Europe. The limiting line of the erratics probably marks the former termination of a great mass of moving ice, and the further extension of the shingle over the plains was possibly due to the action of the multitudinous streams which ran away from the front of this ice-sheet. The chain of the Andes as prolonged through Tierra del Fuego and the islands to the south curves round towards the east in a hook-like manner. The limiting line of the large boulders corresponds in a striking degree with that of the Andes. These facts tend to indicate that during the first Glacial Age the snow and ice which are now limited to the top of the mountains descended some sixty miles into the pampas in the form of a uniform mass, moving outward all the time, and melting away along the line which I have tried to indicate. The ice as it descended caused considerable disruption and erosion of the mountain tops and hills, and carried with it an immense amount of broken debris, which it deposited on the lower lands ; as the ice melted, the abundant streams formed from it carried this material further, rounding off the pebbles as they travelled, and eventually spreading them out over the flattened plains.

Proceeding to the north from the lower portion of the Rio Coyle, one finds first an area of terraces extending back from the river for distances in different places up to six or even ten miles. About ten miles further across the pampa is another scarp-line, about one hundred and fifty feet high, leading up to another pampa, equally as flat as the one we have just left. The line of this pampa scarp differs from those of the terraces in that it does not run parallel to the river, and it has no corresponding scarp equal to it in height on the south side. It is also much too far back to be connected with the river. After travelling another thirty miles or so northward we come to one more scarp, which brings us on to yet another pampa. Now these two latter pampas, in addition to what I have mentioned, also differ from the terraces, in that they possess all the characteristic flatness which I have alluded to ; in fact, they are pampas just as truly as that which we saw north of the Gallegos river. Hence to the north of the Coyle, unlike the same side of the Gallegos river, there are, in addition to the terraces, three distinct

pampas. Now, as we have already seen, the sudden drop from high to low level at the mouth of the Gallegos river probably marks the remains of an old coast-line; so, taking all the facts into consideration, I am inclined to believe that these latter steps belong to the pre-shingle period, and are remains of old coast-lines also. They were formed well back in tertiary times, when the high winds and dry climate prevailed, and they show a steady tendency towards elevation of the land, which, however, was intermittent in its action. Passing now along the north side of the Gallegos river, towards the west, we find that, sixty miles from the coast, the typical pampa still exists in all its flatness, even up to the very edges of the deep cañadones. Another fifteen miles, however, brings about a complete change; here the country begins to rise suddenly fifty to a hundred feet or so, and then goes on for another sixty miles before it reaches the mountains. The surface of this latter portion is completely changed from the pampas below, in that the flatness disappears and an undulatory condition takes its place. In addition, however, great stones appear here also; in fact, we find that this sudden rise in the level of the pampa marks the line I have already indicated as the termination of the erratic boulders. This line of junction between the flat pampa and the undulatory land is as a rule clear to the north of the Gallegos river, and one can trace it without much difficulty. To the south of the river, however, it is not so clear, as two actions have apparently come into play since the great shingle period which have complicated matters: one of these is the elevation of the southern coast-line, and the other is the enormous erosive action of the great river floods. The boulder shingle deposit is, undoubtedly, of glacial origin; and here it would seem that the great undulatory boulder area, the shingle of which runs up to a hundred feet in thickness, is really the remains of a great terminal moraine, and that it marks the limit of the advance of the ice during the first great ice stage.

IV.

The Recent Volcanic Series.

About eighteen miles to the west of the port of Gallegos on the north bank of the river, we find the first evidence of former volcanic activity, and from this point for over a hundred miles in a westerly and south-westerly direction many extensive sheets of lava are to be found spread out over the surface of the plains. There is no very large volcano in this portion of the country; but the number of small cones is immense, and they can be seen dotted all over the pampas as far as one's eye can reach from horizon to horizon. This lava must have resulted from successive eruptions, occurring

during a very long period, as we have cones of all ages, from very weathered ones to others apparently quite recent.[1]

We may begin with a short description of the most recent lava outpouring which I have found in this part of the country.

The Cerro Diablo is a comparatively small and insignificant cone, only a few hundred feet higher than the surrounding plain; its summit consists to a large extent of scoriæ and finely divided cinders; the latter exist in such quantities as to render the ascent rather difficult. Both scoriæ and cinders have a very recent appearance, and give one the impression that the volcano was active at no distant date. The lava-flow from this crater is one of the most extensive in the country; it is fully fifteen miles in length, in many places upwards of fifty feet thick some miles from the cone, and nearer to the latter much more. It runs in all directions over the plain from the Cerro Diablo, and must have been poured out in a very liquid state, as it is found flowing down the small cañadones in minor streams, even nine miles from its point of exit from the vent. The surface is covered by a kind of crust, varying from six inches up to many feet in thickness. Between this crust and the lava beneath there are empty spaces, extending here and there in all directions; these spaces are often so large that several people could go down into them and stand erect, with a roof of lava over their heads.

The lava is deeply fissured everywhere, huge crevasses gaping open, and extending many feet down into the rock. In many cases large portions of the crust have fallen in, revealing deep, gaping holes; in other places, again, the surface is practically unbroken. However, one of the most important points in our present study is that the original cuticle of the lava is absolutely intact and unabraded in the whole of this area; it has a recent appearance, and shows no sign of patination. There is no other deposit overlying any portion of this lava-sheet, and, with the exception of a few bushes growing here and there in the corners, and some ferns, &c., in the cracks, there is practically no vegetation. After carefully examining this lava-sheet, and walking over a considerable portion of it during several days, I have never found a pebble in any place more than ten yards from its edge. At a place called Pali Aike, situated at the side of the Rio Chico, this lava-sheet pours down the cañadones and out into the river valley.

Now, I hope presently to bring evidence to show that the lowest bed of the river valley, with the cañadones running into it, represents the last

[1] On the characters of the lavas, see Olof Bäckström, Petrographische Beschreibung einiger Basalte von Patagonien, &c., Bull. Geol. Inst. of Univ. of Upsala, vol. xiii, p. 115. (1915.)

erosive effort of the last phase of the Ice Age. If this is the case, it will be evident that the lava outpouring of the Cerro Diablo is at least post-Glacial. The other lava-sheets found on the pampas differ considerably from the above. There are no gaping fissures and no open holes to be seen anywhere in the rock, all such having been long ago filled up and obliterated; and there is no intact cuticle, nothing being found but fractured surfaces. Also where they reach the edge of a river valley or cañadon the sheets break off abruptly, and fall in the form of cliffs. All over such lava-sheets a fair amount of recent soil occurs, with abundance of good grass and vegetation; in fact, the hommocky masses already referred to are in many places only seen here and there jutting through the grass.

Except in one or two trifling cases, which I will return to later, no shingle is found on any of the lava-sheets; the soil in which the grass and bushes grow is a rich, black loam, and does not contain any pebbles in its matrix. In the areas between the lava-sheets, where large erratics are lying about here and there all over the surface, none of these erratics consists of lava. Consequently the period of volcanic activity must have had its origin subsequent to the termination of the first great Ice Period. In the summer of 1914 I was fortunate enough to find two places where the typical pampa shingle could be seen under the lava, and, more strange still, in one of these places I found that between the shingle and the lava there was about one hundred and fifty feet or more of a well-stratified rock. This latter, which is of the greatest interest, I hope to describe in a subsequent section of this paper. It was formed long after the shingle was deposited on the pampas. Considerable erosion has occurred in many of the early lava-sheets since their formation. In one place a cañadon, some hundreds of yards wide, and eighty to a hundred feet deep, has been cut through them.

A feature of importance in the present study is that the lava-blocks are often to be found arranged in a peculiar sloping manner, rising towards the east; and on the slope facing west there are usually to be found a number of grooves running up along the stones in an oblique manner. The space between the grooves has always a smooth, ground-down appearance, and the surface is often concave. This grooving and the peculiar lie of the stones are well marked in Pl. VI, fig. 2. This peculiarity of the lava-blocks is found in widely different localities; the grooves always run in the same oblique manner from east to west, and always on the sides of the slopes facing west. The grooves may be seen on the north or south sides of the stones, but are never found on the eastern ends. The direction varies from due east to east-north-east. During several years of residence, I have visited every possible lava-sheet that I could approach in the Gallegos district within eighty miles of the

town, and have travelled many leagues over these rocks. In every place I have studied this grooving, and, as I have said, I have never failed to find it in any locality where there is lava, except in the case of the Cerro Diablo.

V.

Indications of Strong Westerly Winds.

I have had many explanations offered to me as possible causes of the grooving of the stones mentioned in the last section of this paper. The only one, however, which is worthy of note is the action of high westerly winds carrying sand, grit, &c.

One of the most characteristic climatic features at present in Patagonia, particularly during the summer months, is the strong dry winds which blow from the west. These winds blow as a rule about one to two days each week during the summer and autumn. As I have already mentioned, a large amount of sand and dust is carried along, and I have noticed surfaces of dried mud in a valley cut in grooves in the same manner as the stones after a few months of windy weather.

It is noteworthy that the grooves always run up the westerly faces of the stones in an oblique manner towards the east, as would result from westerly winds blowing in dry weather and carrying gritty particles. The fact also that grooves are found down in narrow spaces between stones is strongly in favour of wind action. If, however, we examine recent lava-sheets, such as those from the Cerro Diablo, or if we examine the large blocks which have fallen down from the most recent lava cliffs bounding the present beds of the river valleys, we may search in vain for grooving. I have found abundance of grooving on all the higher levels, but on the lowest and last levels of the river valleys, although I have searched extensively, I have never seen it in its typical and characteristic form. Another point of considerable importance is that in hundreds of localities where this grooving is found a peculiar rusty patination of the surface occurs, in marked contrast with the clean black stone revealed when the grooved surface is chipped off with a hammer. The grooved surface is now becoming weathered off the stones and not weathered on. In many localities the grooved surfaces have been overgrown with lichens, mosses, and other vegetable matter; and they are often hidden away behind bushes and shrubs, which are growing with ease in front. The evidence, consequently, seems to point to the fact that this grooved condition of the stones was brought about during some former geological period, and was not produced since the river beds were cut down to their present levels.

From the above we see that at some period during the time when the river valleys were being cut out, and while the rivers were still exercising an erosive action, high dry westerly winds blew over the country with great violence. Volumes of gritty particles were carried along, and all rock surfaces exposed were extensively eroded. In some places there are large, hard basaltic fragments, which must have lost upwards of a third of their bulk in this manner, and in more than one place a stone occurs which, from its shape and general direction of its grain, must have had fully a ton weight or more of its substance removed by wind action. On going through the volcanic area, I was struck by the fact that quite a number of the cones had a long slope upwards in one direction, and a steeper descent on the other side; for instance, in the chain of the North Hills, out of eight hills, two had this slope. I have also noticed this feature in several other places, and the highest side lies always towards the east. The central craters in these sloping cones are often found to a large extent filled up, and the edges of the rims are as a rule rounded. I now conclude that the high wind was the cause of this phenomenon also. We have already seen that we have reason to believe that the great flattened condition of the pampas was produced by high winds in pre-glacial times. We see now that during inter-glacial times there were periods also when high winds prevailed. Before concluding, I wish to state one objection. At a place on the Gallegos Rio Chico, situated about thirty-five miles from its mouth, the river curves round and runs in a north-westerly direction. The terrace on the left bank is here almost a hundred feet above the bed of the river valley, and it is capped with lava, which falls in the form of a clean cliff a short distance from the top. On the summit of this cliff the usual wind-grooving runs from behind right out to the edge, and it is well marked all along. When climbing this cliff one morning, I was suddenly startled by seeing the typical grooves running down its face almost perpendicularly. These facts are a difficulty for the wind theory, as it is impossible to conceive that hard particles travelling along the top with such force as to cut the stones would not, by virtue of their momentum, be carried clear of the edge in their descent. I will return to this subject later on, when I hope to show that far outside the limits of the great moving ice-sheet there was also another form of local ice-action at work.

VI.

Origin of the Terraces in Spring Floods of the Ice Age.

If we take for examination any typical portion of one of the river valleys, such as that of the Gallegos river, the floor of the valley is, perhaps, a mile

wide, in some places more, in some less, and the surface is practically level, no portion of it being more than ten to fifteen feet above the river. The sides of this valley are bounded by steep rising banks, probably eighty feet in height, which mark the beginnings of the first terraces. The floor is in most places covered with a rich black soil, on which grows an abundance of rank vegetation, except in these places which have been eaten down from over-stocking with animals. Small lakes occur here and there, and the river winds about through the valley in a very sluggish manner, now on one side and now on the other. Patches of swamp lie in different directions, yet in no place is the river very deep; in fact, almost every half mile or so it is capable of being forded. The river is always shifting its position through the valley, and as it cuts a new course the old one becomes first a lagoon, afterwards a swamp, and finally becomes obliterated by vegetation, mud, and various kinds of rubbish which have fallen in. The river during the ordinary dry weather in summer runs between perpendicular banks, is perhaps about five feet below the level of the main valley, and is anything from fifty to a hundred yards in breadth. If, however, we visit it during the month of September, which is the spring of the year in Patagonia, we shall probably find that it has risen considerably, possibly flowing over the banks in places and flooding parts of the valley. These spring floods are a marked feature in this country; they vary much in different years and in different rivers, being sometimes hardly perceptible, while at other times they fill the whole valley from side to side with one great river. Seven or eight years may pass during which there are practically no floods or only very slight ones, and this period may be followed by one or two years when the whole valley may be filled. When the river rises sufficiently high to flood the whole valley, in about a week or two it usually recedes once more between its banks; it may, however, remain in a flooded condition in its own channel for more than a month. After the flood has gone down it is surprising how little change has taken place. We may find a few bits of twig deposited here and there along the sides, and some mud in odd places; but in most localities the valley is as it was before; in fact, if any alteration has taken place, it is that the river valley now contains somewhat more soil than it had formerly. These spring floods are always the result of the melting of the snow on the high lands towards the west, and are, consequently, greatest in those years when there is most snow. Any erosion of the valley during flood-time is more than compensated for by the deposit carried down from above, and, as erosion by wind does not take place on account of the amount of vegetation which protects the surface, we have reason to believe that under the present conditions the level of the valley is slowly rising. At any rate, as climatic

conditions exist at present, no great erosion is taking place in the river valleys; and it is quite possible, as far as we can see, that the beds of the rivers stood practically at the same level many thousands of years ago as they do to-day. The hilltops and mountains to the west are, of course, becoming worn away, but the lowlands and valleys, wherever the surface is protected by vegetation, are probably, if anything, rising. I have found abundance of evidence of this latter fact in many places, in the shape of bones of recent animals, such as guanaco, &c., some feet below the surface of the soil in the valleys. If we dig down through any of the river valleys, some distance up from the sea, we pass through a considerable depth of shingle and sand, very similar to what we find on the pampa, perhaps fifteen or twenty feet before we come on the actual tertiary rock-floor. We also find in places a considerable depth of mud and black soil where the gradient of the valley is slight; in a tributary dry cañadon, where the gradient is more marked, there is not as a rule much black soil or mud; but even here the floor of the cañadon is covered by a layer of, perhaps, fifteen to twenty feet of sandy shingle. In very few cases—and this is a very important fact—is the tertiary rock-floor of the cañadon exposed to view, the only exceptions being those cañadones which have very steep gradients, and which drain very extensive areas. All the river valleys and cañadones in southern Patagonia, with the exception of the Santa Cruz river, are subject to occasional spring floods. Those floods vary in different localities, and in different years, but they are always found at times right through the country.

The Santa Cruz river is an exception, as it does not begin to rise until the summer, and does not reach its height till well into the autumn. The reason for this is that this river takes its origin in some large lakes situated well in between the cordilleras, and, as the snow on the latter melts much later than that which falls on the plains, the floods are consequently delayed. Most of the terminal branches of the Gallegos river rise in the plains; one or two of them, however, extend as far as the cordilleras, and consequently occasional summer or even autumn floods occur in the Gallegos river after periods of hot weather, when additional snow has melted on the mountains. The local rainfall has very little effect on the floods in this country. Even after several days of heavy rain, such as occur occasionally, although the small streams may be slightly increased in amount, the rivers show practically no rise. Rain never fills up the lagoons, and experienced farmers will tell you that without snow they never have their land properly supplied with water. Any rain falling on the shingle-surface of the country will sink in unless the surface is made water-tight by being frozen. Now, when the snow begins to melt in the spring, the superficial layer of the soil is actually frozen, so that

the water runs over it and escapes, some of it into the lagoons and the rest into the cañadones, through which it eventually makes its way to the rivers. Thus the essential factor in the production of floods is not rain, but snow, and these floods are always found in the spring of the year, when the snow melts. The snow which falls on the plains and lowlands is also most productive of floods. If the climatic conditions as they exist at present became changed in such a way that the winter snows were increased to four or five times their present amount, the spring floods would be correspondingly increased, and, instead of having a depositing action, as they have at present, they would first clear all the recent soil out of the valley, and next all the gravel and sand, and finally the bed-rock would be cut into, so that the river valley would once more become deepened, and probably new terraces would come into existence. This sequence of events, namely, a change from a period of mild climate such as exists at present to one when the snow-fall was considerably increased and the spring floods were hugely augmented, probably occurred several times in the past, and it is likely that all the terraced river valleys were cut down intermittently in this way. It seems, then, that the present spring floods are only the shrunken remnants of what once existed on a grand scale, and that all the great river valleys and cañadones were originally cut out by the action of spring floods, due to the melting of large masses of snow and ice.

We are now in a position to adopt certain rough divisions of the past history of Southern Patagonia as far back as our story goes. We may divide it into, first, a pre-shingle period, when wind was the dominant eroding force; second, a shingle period, which probably was identical with the first great advance of the ice—no river valleys or cañadones existed then; third, a long period of erosion by water, which was subject to considerable oscillations due to alternations in the climatic conditions; and, fourth, a genial period, which is still going on, and which has probably existed for some thousands of years.

VII.

Erosion subsequent to the outpouring of the Lava.

The surface of a river terrace is covered with sand and shingle, very similar to that which is found on the pampa, of about the same thickness, and distributed practically as evenly. If, however, a cañadon or gully which cuts into one of these terraces be examined, it will be found that this shingle-layer is somewhat different. A cutting running into one of the terraces near the mouth of the Coyle river shows marked current bedding, the pebbles being sorted out into irregular layers, and the spaces between being filled

with sandy earth; the latter also exhibits false bedding in thin layers. This arrangement of the terrace shingle gives one the impression of a great, fairly rapidly running river carrying with it a large amount of silt. The terrace which we are now considering, with its fellow on the opposite side, would make a river valley perhaps five or six miles in breadth; and when we consider that the whole of this horizon is covered with a layer of sandy shingle, averaging about fifteen feet in thickness, we can form an idea of the size of the river and the magnitude of the floods which existed in former times. This terrace is about two hundred feet below the main pampa level; consequently the river valley of which it once formed the floor must have been cut down very considerably through tertiary rocks before this shingle was deposited. Now on this same terrace we find an occasional flat-topped hill, rising to the level of the main pampa, and the hill is covered with pampa shingle, which shows that the cutting-down action of the valley must have occurred subsequent to the pampa-shingle period, and the terrace shingle must be of far later date than the first Ice Age. The first phase was a cutting one, when the floods were enormous, and all the materials eroded from the valleys were swept to sea; the second occurred when the floods had considerably abated and the cutting action had been replaced by deposition. The map of this part of Patagonia shows that from the top of the highest ridge of the Andes to the Atlantic is not more than one hundred and eighty miles, and, as this narrow strip is intersected every thirty miles or so by a huge river valley with branching cañadones, it seems wonderful that such an area could have collected enough water to cause the floods we have been considering. If, however, this country was once covered with a great mantle of snow and ice which had been accumulating for centuries, and when this had reached its climax the climate rapidly began to get warmer, enormous floods would be prevalent every spring; this flood-epoch would last until the accumulated snow and ice would disappear in the spring and summer. Now at first during this period the pampas and highlands would be protected by a deep layer of ice; consequently they would not suffer much erosion, but the whole force of the floods would be concentrated on the floors and sides of the river valleys, with the result that the latter would be eaten down and the debris swept away to sea. Later on, when the climate had become still more approximated to what we have at the present day, and the pampas and highlands had become denuded of their protecting mantle of ice, the floods would begin to wash down huge quantities of shingle and sand into the river valleys. The force of the floods having in the meantime considerably abated, this deposit would accumulate until the floods died down to their present-day insignificance, when, the climate having become mild, vegetation would spring up

all over the country and protect the surface against further erosion. The pampas are sometimes frozen when the water is running freely in the river valleys; and I may mention a very striking example of this which I myself witnessed. On the north side of the Gallegos river, almost in front of the town, there is a huge cañadon which runs back about two and a half miles; it is very broad, and has several tributary cañadones, one of which, after rising rather abruptly, ends on the pampa. In the end of June, 1913, I was going to Coyle, and left the river-side at 9 a.m. A misty rain was then falling, and quite a fair-sized little river was running down the cañadon; there was no snow below, and everything was wet and sloppy. The stream continued, although gradually diminishing in size, as I went up, until I got within fifty feet of the top, when it ended in snow and ice; the mist had by this time turned into sleet, and I was surprised on going about two hundred yards further and reaching the pampa to find that this latter had in its turn changed to snow. I was also surprised to find the pampa dry, hard, and covered with snow and ice, with no sign of thaw. My horses here gave in, and I was compelled to return; and, when I came a half a mile down the cañadon, I found everything was as before—the same running stream, the same mud, and the same misty rain. It is also a well-known fact that after a severe winter the snow and ice will have completely disappeared from the pampas near the sea fully a month, if not more, before they begin to melt on the same levels sixty to seventy miles inland.

These facts are very significant, and indicate that when the great ice mantle began to melt it did so first along the sea-coast and in some low-level bay or bight. This bay would be cut out first to a considerable extent, and would eventually mark the starting-point of a river which would cut its way back into the high ground as the ice receded. According to this method of reasoning, it would seem that the shingle covering the river terrace we have been considering came down towards the end of a flood period, and was deposited at a time which came immediately before a phase of mild climate such as exists to-day. All along the Gallegos river valley we find numerous lava-sheets; some of them are on the pampa, but most of them are found capping the terraces, even down to the lowest. Now these lava-sheets, except where they are broken up by former ice or water action, show very even and compact distribution, and seem to have been poured out over a dry-land surface; for, had there been floods at the time of the volcanic outpourings, the lava would have been immediately cooled as it met the water, forming huge frizzled-up heaps, and would not have become spread out in thin, hard, compact sheets. Now, except in one instance in the cañadon Guer Aike, I have not met with any deposit of shingle on the surface of any of these lava-sheets—at

least in the lower seventy miles of the river valley; on the other hand, the lava lies on the shingle in more than one place, and I have reason to believe that it does so in every instance. This would prove the lava to be the younger rock of the two, so that, if the lava corresponds with a resting phase of the river valley between two phases of ice and flood, the shingle must have come at the end of the flood or before the resting phase. The history of a river valley in this region may be divided into four periods as follows:—first, an ice phase; second, a flood-cutting phase; third, a flood-depositing phase; and fourth, a resting phase. If now each terrace marks the base of a former river valley, we should expect this sequence of events to have been repeated as often as there are river terraces.

The further discussion of this very important and fascinating subject I must leave until I am in a position to obtain additional evidence. It seems clear that a great period of ice-advance was followed by a long period of erosion by water; this flood period was intimately connected with glacial action, and the huge spring and summer floods were due to a much greater winter snow-fall in former times.

There is a terrace along the Gallegos river, which is covered for a considerable distance (half a mile or more) with a mass of broken debris, consisting chiefly of huge angular fragments of basalt up to six feet or more in length. Packed between these basaltic fragments, will be found a certain amount of pampa shingle, many of the stones of which are wedged in such a way that it is clear that they came there at the same time and with the basaltic fragments. This mass of debris lies on a lava-sheet, which shows a different composition and structure from the great basaltic blocks above, and the whole mass of this deposit was evidently carried from another locality, and heaped up over the lava-sheet in question. A little further up the valley the river makes a well-marked bend round to the north, and here, on the terrace, is a peculiar knob standing by itself. This is the remnant of a lava-sheet, which once covered this terrace up to the level of its top. It is about thirty feet in height, and is removed upwards of half a mile from the nearest edge of the sheet, of which it originally formed a part. Hence extensive surface-erosion of lava occurred here at one time, and it is more than probable that it was from this surface that the lava blocks were derived which we saw heaped up on the lava-sheet below. We see from this that during the cutting down of the river valleys there are two forms of erosion of lava—namely, the ordinary erosion of the sides of the sheet during the cutting down and deepening of the river valleys, and also a form of surface-erosion, where great areas of the surface of a sheet were broken up and carried away in huge fragments. A few miles down the river, at a place

called Buitreras, there are some wonderful examples of lava erosion. In a general bird's-eye view of the river valley, looking westwards from the southern edge of the river, we see in the distance a volcanic cone forming part of the edge of the river valley. It has been cut clean in two through its centre, like an apple divided through its middle by a knife.

Pl. VII, fig. 3, gives a nearer view of this cone; it is about three hundred feet high, and of the southern half nothing whatsoever remains. Across the river valley, however, which is here a few hundred yards wide, the edge of a lava-sheet is found, which was probably at one time continuous with this cone. This means that the river valley, which has here been cut down to a depth of over eighty feet, has required for its formation the removal of not only a considerable lava-sheet, but also of half of a volcano cone three hundred feet high. Now, if we follow down the Gallegos river to its mouth some fifty miles away, we find practically not a single block of lava bigger than a few inches in length, and even these are few and far between. The river valley is throughout covered with the usual shingle, sand, and silt. Millions of tons of solid hard basalt have been removed from this area in some comparatively recent geological time, and there is no trace of them in the river valley below. The terrace which has been here cut through is the lowest in the Gallegos river valley, and consequently represents the erosive action, if not of the latest, at least of one of the latest flood periods. The basalt here is a very hard stone, and we can only wonder what has become of the millions of tons which have been torn out of this place and swept away. They may be buried in the floor of the river valley; but, if so, heaps of them should show above the surface in some localities. This is not the case, and we may consequently conclude that these great lava blocks have either been ground into fine material or carried bodily away to sea. It is difficult to imagine that these huge fragments, many of them weighing many tons, could have been ground up into fine shingle during the last flood period. I will here quote from my note-book: "25th March, 1915. The western end of the Buitreras table, although consisting of bed-rock (sheet of basalt), has its surface very broken. Curious hollows, ending blindly towards the west, but often opening towards the east, in the form of cañadones are found, and some small hollows are found without any opening. Some of these cañadones, which are always blind towards the west, are cut deeply back into the lava towards the west, and have some small amount of shingle on their bottoms. Towards the eastern end of the western half of this table there is extensive surface-erosion of the lava; the latter seems to have been eaten into by the cañadones mentioned; on the sides of some of these there are actual cliffs of lava up to twenty feet high." The Buitreras table here mentioned is an elliptical-

shaped flat lava-topped piece of ground, situated on the south bank of the Gallegos river, opposite the Buitreras cone. It is about two miles long by, perhaps, half a mile broad. It is bounded on the north by the Gallegos river, and on the south by a large cañadon over two hundred yards in breadth, which separates it from another extensive lava-sheet to the south. It falls abruptly to the west, but gradually to the east. The lava ridge is here about ninety feet high above the river valley, and the lava-sheet, which is still practically intact on the western end, is completely broken up on the eastern portion. On carefully examining it, we will find that a peculiar ridge of more or less intact lava extends down as a fringe along the northern edge of the table for a little distance. One of the above-mentioned blind cañadones extends up behind this ridge to the south. The Buitreras table has thus suffered a considerable amount of surface-erosion during late glacial times; and, although the erosion is almost altogether confined to the eastern two-thirds of the table, the eroded area encroaches on the intact western end in the form of a series of bights into the lava-sheet. There are also some hollows eaten out of the latter, which end blindly in all directions. What then was the agent which produced this condition of surface-erosion, which is by no means limited to this particular place? There are no signs of sea-shells, or any form of beach; besides, all the great basaltic fragments are, as a rule, angular, and not rounded as they would have been if the sea had been playing on them for any length of time. A great flood might have been the cause; but such is difficult to imagine. What then was the state of affairs in the Buitreras area in the particular time that we are considering?

I have imagined to myself a great mass of snow gradually settling by pressure into ice, accumulating for centuries generally over the whole country, particularly on the high pampas. This went on to such an extent that the river valleys became obliterated by ice. The country was so flat that this ice-sheet had no tendency to move, but simply lay there as a stagnant mass in the area in which it was formed. At least its movement was so slight that it caused no moraine formation, and no scratching of the stones. As a consequence of the same stationary condition, the ice-mass was clean, and held practically no picked-up material, except perhaps a little in its lower stratum. Then occurred a change of climate, which set in rather rapidly, with the result that this great ice-sheet began to melt away. Hot summers set in, during which huge floods occurred, masses of water poured down through large crevasses, producing extensive sub-glacial erosion, and from the eastern fringe of the ice-mass immense blocks of ice became broken off, and floated away to sea on the waters. As they broke away, they carried with them large pieces of the lava, which separated along with them. When the

floods were at their height, these lava-laden icebergs floated away to sea, as I have said. However, when the floods diminished, most of the icebergs grounded, and melted away *in situ*, shedding their lava debris. This explanation seems the only one that accounts for the condition of affairs found in this locality.

If we now pass downwards towards the east, a few miles from the Buitreras, the high pampa level to the south is seen to be capped to a considerable extent with sheets of lava, which have been poured out from small cones which surmount it close by. After we pass along the highest cliff, or barranca, as it is called, for about two and a half miles below the Buitreras, this lava-topped cliff takes a sudden bend to the south, at right angles to the line of the river-valley. It runs in for about half a mile, and again runs towards the east. During this half-mile course, the lava-cliff faces east, and consequently has its back up stream. For several years I could not understand how even a huge river filling the whole valley, here about five miles wide, could turn this corner and undermine the lava-sheet to such an extent as to cause this cliff. There is no sign whatever of a shingle beach at the base, and all the fragments are angular, and show no signs of rounding, as they would if the sea had been acting on them for a long period. On the contrary, the whole place gives the impression of the cliff having been cut down by a large mass of water pouring over it from behind. Now, this particular cliff exists on the northern edge of the narrow tongue of pampa which I have already mentioned as extending down between the Gallegos river and the Rio Chico. This tongue is extensively cut into, and forms altogether a very small collecting area. The greatest rainfall which could be imagined would not produce sufficient running water to cut down these lava-sheets in the manner which is found to have taken place. A huge accumulation of snow, piled hundreds of feet high on top of this table, and then rapidly melting, might, however, produce sufficient running water to bring about these changes.

Now, if the process outlined above was the causative fact of the surface conditions, the result would be that during a hot summer large volumes of water would be formed by melting all over the ice-sheet. This water would flow towards the east, and would fall over its limiting edge in an extensive series of cascades. Now, at first, while the ice-sheet was still very thick, these cascades, falling as they would from a considerable height, would resemble a number of miniature Niagaras, and would produce much erosion of the surface of the land on which they fall. They would also tend to hasten the backward recession of the ice-sheet by breaking away its edge. Huge fissures extending downwards through the ice as large blocks of the

latter became broken away and detached would also lead to local attack on the underlying lava, which might in that way become very much broken. A subsequent severe winter might now freeze lava-blocks and ice into one compact mass to such an extent that the ensuing summer floods might pick up large pieces of it and float them away. As, however, the ice-sheet as it recedes is also all the time diminishing in thickness, a point will sooner or later be reached when the ice-sheet will become so attenuated that its floods are negligible, and have no further eroding action. Such a condition of affairs was probably reached over the Buitreras table when the edge of the ice-sheet reached the point already indicated near its western end.

It must not be supposed, however, that the series of events which ultimately took place was as simple as I have outlined above. It is much more probable that during the whole action there were extensive oscillations of temperature, not only from summer to winter, but also greater variations when several seasons of comparatively hot weather alternated with other long periods of cold. The idea which I have outlined seems to me the most likely explanation of the phenomena which I have observed.

VIII.

The Problem of the Bajos.

As I said in the first section, if we travel any considerable distance over the pampas we are sure to come across an occasional great hollow which is not a river-valley. A typical example is the Bajo de las Tres Lagunas, on the second pampas to the north of the Coyle river. The pampa here is upwards of a thousand feet above the sea, and has all the characteristic flatness already noted, so much so that we are almost on the edge of the bajo before we are aware of its existence. This bajo is elliptical in shape, with the long axis running east and west; it is about five miles long, two broad, and the base of it is four hundred feet below the general level of the plain. The western extremity is deeper than the eastern end, and the three salt lagoons are situated in the western half. At the sides of these lagoons, which in the summer and autumn are practically solid salt, there are to be seen a number of springs; some of these ooze up through the mud, and are covered with a dry crust, which renders them very dangerous, as animals often sink in, and are unable to extricate themselves. The eastern end of the bajo is found to slope more gradually than the rest of the circumference, which falls rather abruptly. As a rule there are no very great cañadones running into it; but a number of semi-cup-shaped bights cut into the rim all along. However, in one or two places a cañadon,

half a mile to a mile in length, can be seen. Some of these cañadones are more like arms of the bajo, as the main floor-level of the bajo extends into them for almost their whole extent, or at least the floor of these arms is often not much higher than the main floor. This bajo was formed by erosion, and not by subsidence, since the strata of tertiary rock crop out on the sides, and are clean cut off at their edges, as they are on the cliffs along the Atlantic coast. As a rule, between the bights already mentioned ridges extend downwards and outwards into the bajo from the top. In some places these ridges form three irregular steps; these latter, however, although a rough attempt at terracing, are not anything like so well marked as the terraces along the river-valleys. In some places the ridges are fairly broad, whereas in others the sides of the bajo are cut every hundred metres or so by in-running cañadones. The lower terrace is in one place so cut that it shows two or three little rounded hills, with flat tops, these being so equal and even in height that they give the idea of their marking the level of the floor as it existed at a former time. The pampa on all sides of the top of the bajo is equally level, and on the east side there is no more sign of a hill than there is on the west, so that of the great mass of material which once filled up this hollow not a trace remains. The three salt lagoons, from which the bajo takes its name, only occupy a small portion of the floor, the remainder being covered with bush, grass, and other vegetation. The cañadones and bights, already described, leading into this bajo are very similar to the cañadones found elsewhere; they are clothed in vegetation, and show, like the others, practically no signs of present-day erosion. Hence it is probable that the Bajo de las Tres Lagunas has not altered much during recent centuries.

Now, all the characteristics of this bajo are to be found also, to a certain extent, in all the others. Half a mile to the eastern end of this great valley there is another one, which is very much smaller in size and depth; this latter is about three-quarters of a mile long, and about three hundred yards broad, and about eighty feet deep; at its western end a bare, gravelly patch of a few acres in extent marks the situation of a small lagoon, which exists, as a rule, only in spring and early summer. The centre of this patch is covered with dry mud, and there is no sign of vegetation on any portion of it. There is no attempt at terracing in this bajo, and it would seem to consist of one horizon only, although, like the other, its lower portion is the western end, and it slopes slightly upwards towards the east. All the floor not occupied by the bare patch already mentioned is covered by the same vegetation as is found elsewhere, and shows no sign of recent erosion. Everywhere over the pampas semi-bare patches occur, which are often only

a few feet below the main level; these may vary from a hundred yards or so up to four or five hundred in breadth, and are covered by short, fine grass. They have often in their centres patches of bare shingle, and no bush is found growing in any portion of them. These patches mark the sites of spring lagoons, and their semi-bareness is due to the partial sterilization of the surface produced by the water, which lies on them at times for some months. These spring lagoons are only formed after severe winters, when there is heavy snow, and sometimes they are absent for a period of six or seven years. From this it would seem that we meet all grades of bajos, from the merest shallow semi-bare patches, only a few feet below the level of the main pampa, down to great hollows several leagues in length and hundreds of feet in depth. On the floor of some of these bajos we find a class of hill which rises abruptly in the west and falls gradually towards the east. These hills, of which there are a number in some bajos, are capped with a thin layer of shingle, and their tops would seem to mark a former horizon in the formation of the valley. Bajos are found, not only on the main pampa, but on all the lower horizons, except the floors of the river-valleys. On the side of a bajo situated on the third terrace above the floor of the Coyle valley is a very well-marked terrace about sixty feet above the lagoon, which was, at the time of my visit, of pure salt; its top is as flat and its edge is as clean cut as any of those found on the sides of the river valleys. Barometrical reading showed the surface of the lagoon in the bajo to be only twenty feet above the Coyle river.

It has been suggested that these bajos probably originated through a combination of wind and water action. The water remains in a slight hollow for a few months after the melting of the snow in the spring, and causes destruction of the vegetation which normally protects the surface. The soil beneath is thereby exposed, so that, when the water has dried up, the winds, which blow very strongly in summer, attack it, eat into it, and blow it away. The next season the lagoon is a little larger, more vegetation is destroyed, more earth is blown out, and the hollow becomes deeper. This goes on year after year until a huge bajo is formed. This explanation is very plausible, and seems to agree with the facts in many instances; in fact, I may say that I have seen in more than one place this mode of action actually working. For instance, near the town of Gallegos at least two such places occur, where the dust and sand of the hollows is found to be heaped up on the eastern sides in the form of mounds. I also know one small bajo on the high pampa between Gallegos and Coyle where such a mound can be seen on the east side of the hollow. In the vast majority of instances, however, no mounds or elevations can be seen on the sides of the bajos, and no scooping out seems to be occurring to-day.

The great difficulty in the way of accepting the foregoing theory in its entirety is the presence of the shingle; and it seems unthinkable to me that wind, even assisted by water, could produce this great erosion of a surface protected by a deposit of fifteen feet of pebbles, many of them up to eight or nine inches in length. Then it may also be asked why should this erosive action only affect isolated patches when the great portion of the area is untouched? The tertiary rock below is of a clayey nature, and quite insoluble; it would consequently not suffer any erosion under fifteen feet of shingle and sand. If by any chance certain patches of the pampa remained uncovered when the shingle was washed down from the first great ice-sheet, these patches would then be exposed to the action of wind and water, and bajos would soon result. I was talking this matter over with a friend one evening, and he suggested that perhaps there might have been a few small hills remaining in the first instance which had resisted the great planing influence which was operating in pre-shingle times, and that these hills, being higher than the surrounding plains, were left uncovered when the shingle was washed over the country generally. This explanation would account for all the facts observed, and I now beg to put it forward, with all due reserve, as a working hypothesis. There is, however, one serious objection to this idea: there is a hill, or rather a small tableland, situated on the main pampa to the north of the Gallegos river; it falls all round, particularly towards the west, to the extent of over forty feet, and yet it is covered by the same shingle, and to the same extent, as is found on the rest of the plains. It may consequently be asked why should slight elevation above the surface render the one set of hills immune from shingle deposit, when this plateau, which is fully forty feet above the main plain, is covered completely?

There seems little doubt that some of the bajos must have had their origin well back in inter-glacial times, as can be seen from their huge extent, the fact that there is more than one horizon in them, and that, as climatic conditions prevail at present, they do not seem to be suffering any marked erosion. Since they are found on all the river-valley horizons, except the lowest, factors would seem to have been present for their production in all the inter-glacial periods; these factors, moreover, were evidently absent since the last retreat of the ice.

There is yet another solution of the problem that I regard as the most satisfactory of all. The stagnating ice-mass postulated in Section VII would give rise to localized and often broad-fronted waterfalls during its epoch of rapid melting. The bajo may be regarded as a large pot-hole, or, rather, a vast representative of the pools in a stream with occasional waterfalls. Such pools are often deep at the head and shallow at the foot, and a bajo fifteen

miles broad and thirty miles or more in length none the less presents striking analogies with the miniature hollows eroded in the floors of ordinary streams. It may be once more pointed out that the thickness of the mass of stagnating ice resting on the pampa provided a very effective head for the water pouring in Niagara-like cascades from its surface. I have also found in one place a series of bajos extending in an irregular line from west to east for thirty or more miles. In some instances the bajos are found opening one into the other, while in others a narrow strip of intact pampa may separate them. Such series often occur, I am informed, in other parts of the country also.

IX.

The Buitreras Bed.

As I have already said, the lava in this part of Patagonia is practically always found lying superficial to the shingle, and consequently it is believed to have been poured out after the pampa shingle was distributed. I was consequently somewhat startled to find well-marked sedimentary rock between two layers of lava running out from the cone shown in fig. 3, which is situated at the side of the Gallegos river, about fifty-five miles from its mouth, at a place called the Buitreras. On close examination, however, it was found that this rock differs considerably from any of the tertiary deposits. It is of a coarse sandy grain, generally of a yellowish colour; in some places it would seem to consist of volcanic tuff, and in most places is stratified in thin layers from one to a few inches in thickness; but the most striking fact is that it has not only an occasional angular fragment of lava embedded here and there in its matrix, but also a considerable number of typical pampa pebbles. These pebbles, in the exposure at the side of the Buitreras cone, are in all the varieties and sizes generally seen on the pampa, and are embedded in the rock in all the levels which here crop out. About a mile and a half up along the same side the high river bank juts out at right angles to its main course for a short distance. The top of the bank is here about 170 feet above the river, and consists almost exclusively of material similar to that already described, except that there are neither pebble nor lava blocks embedded in it. It also lies above and below a sheet of lava which crops out more or less in its middle. Along this same bank a few hundred yards further the ground rises for a short distance to the level of the main pampa, and shows the usual pampa shingle on the top; in fact, it has all the characteristics of an isolated flat-topped hill, and its face, as it borders the river from summit to base, consists of the same class of rock found opposite Gallegos and along the Atlantic coast. In other words, it is typical tertiary rock. At the same place where

this rock was observed, although most of it exhibits well-marked true bedding with comparatively thin layers, occasionally here and there well-marked false bedding occurs, showing that at times at least there was running water when the formation was being deposited. I was fortunate enough to find in one place in this locality the clear line of junction between this rock and the tertiary rock, and the rock we are now considering was found to lie unconformably on the latter; in fact, it would seem that it was deposited in a huge basin scooped out of the older tertiary rock.

It is, as a rule, impossible to see what this formation rests on, as there is such a heap of rubbish generally at the bases of the cliffs. I noticed, however, all along the locality where it is found that there is a line of springs cropping out from the valley banks about ten to twenty feet above the river. This would indicate that this rock lies on shingle. In one or two places I actually found the shingle on which it lay, and it was of the usual pampa type. I have given the name of Buitreras Beds to this formation. I traced it for upwards of twelve miles along the south side of the Gallegos river valley, and it probably runs much further. At the mouth of the Gallegos Chico it is found lying directly under a huge sheet of lava which caps a table three hundred feet high. It is here over two hundred feet thick, and at the back of Bella Vista, a few miles further along, I found it up to four hundred feet above the river valley. The fact that this formation was deposited in a great hollow scooped out of the tertiary rock, and lies on a layer of shingle of the pampa type, indicates that it is of a comparatively recent origin, and was formed after the shingle was spread over the pampas. As the base of this bed is only a few feet above the floor of the present river valley, the pampa must have been cut down at least three hundred feet before the Buitreras bed began to be deposited. At least one outpouring of the lava occurred during the time when this bed was being formed, and one river terrace came into existence. From these facts it would seem that the Buitreras beds were deposited during inter-glacial times; and, although some of the deposit may have been formed on the bottom of a lagoon, some at least was formed under running water, as typical current-bedding can be seen in places. It is evident also from the angular fragments of lava found here and there embedded in it that semi-glacial conditions must have prevailed at least during a portion of the time, as these blocks were probably carried by ice and dropped on the bottom of either a lagoon or a large slowly running river.

The lava sheet, which extends through it as an even, horizontal, compact layer for some miles, proves that there was one temporary interruption in the deposition, if not more, and that during that interruption the bottom of the lagoon or

river was dry. We find that the Buitreras beds have in places been cut down a certain distance, when there was a volcanic outbreak and a lava sheet was poured over them; a terrace which had been formed at the mouth of Gallegos Chico was in its turn cut further down by a subsequent action. This extensive terrace abuts, not only on the Gallegos Chico, but on the Gallegos river also, and indicates that there were at least two periods of cutting and probably one of glaciation since the Buitreras beds were formed. Further study of this interesting deposit shows that it has suffered extensive erosion since it was laid down; in fact, only a few isolated patches remain here and there at the sides of the huge valley that was once filled with it. It must have been upwards of three hundred feet thick, and have extended for at least fifteen miles. At the side of the Gallegos Chico (a small river which joins the Gallegos proper at a place called Bella Vista) the Buitreras beds were cut down some 150 feet, and a sheet of lava was poured over them. This latter was further cut through by the Gallegos Chico river another eighty feet, until the tertiary rock was reached and the floor lowered to its present level; and then, as I will show later, a glacier descended into this last river valley, and filled its mouth completely with a terminal moraine. Finally, this moraine has now in turn been cut through by the Gallegos Chico as it runs to-day. The past history of this valley was, then, something as follows:— First, the great shingle period, then a great period of erosion by floods, which may or may not have been intermittent; this lasted until the river valley was cut down to almost its present level. Then occurred a long period of deposition, which was probably intermittent, and during which there was at least one considerable outburst of volcanic activity. When this deposition had been completed, and between two and three hundred or more feet of rock had been formed, there occurred once more a long period of erosion by water, which probably had two or three breaks, as, although there is only one terrace to be seen in the valley of the Gallegos Chico, yet a little lower down there are two more or less distinct terraces. Now, if each of these intermissions of erosion occurred in the manner already described, it appears that there were a considerable number of advanced recessions of the ice in this valley. The cause of the deposition producing the Buitreras beds is obscure. There is no trace of a dam across the river valley lower down which might have caused a great lagoon behind it. If during a subsidence the sea came further up the river valley, the current of the flood-water would have been considerably slackened, and sedimentation would have taken place; a bar might have also been formed and have helped the sedimentation. I did not, however, find any trace of such bar or any evidence of marine formation, so I have been consequently compelled to defer the further consideration of the subject until I am in a position to obtain more evidence.

X.

Summary of Conclusions.

We are now in a position to make a general survey of the work we have gone through, and, as we saw at first, the evidence at our disposal leads us to believe that, after a long period of dry climate with high westerly winds, probably in later tertiary times, the country to the north of the lower reaches of the Gallegos river became so levelled off that not a hillock practically could be found for hundreds of miles. The surface was as level as the sea, and if any inclination existed it was a slight fall from the mountains in the west towards the Atlantic. During this time the land in question was slowly rising, but not at a uniform rate, since we find three well-marked steps from north to south, indicating three old coast-lines. The pampas between Gallegos and Coyle towards the end of this period had partly subsided again, and portion of the land at Cape Fairweather was slightly below the sea-level. When things had reached this point, a change occurred, the climate suddenly began to get colder, and the ice, which was heretofore limited to the higher levels of the mountains, began to descend into the plains. As the ice descended it caused considerable smashing up of the rocks, and it carried a huge quantity of broken debris with it. All this time the climate was getting colder and colder, so that the spring floods were not excessive, and consequently had no great eroding power. The huge quantities of broken debris carried down by this ice-sheet became deposited partly under it and partly along its termination; this limit is shown by a line marked on the map. The spring and summer waters, melting away from this great ice-mass, formed slowly running and expanded streams, and, as the country was one huge slightly inclined plain, these streams could not follow any definite valley, but ran broadcast over the country. They carried with them much of the finer sand and shingle which the ice had brought to its limits, but left all the large blocks behind. This condition of affairs lasted until the pampas were covered with a layer of shingle, which extended right to the Atlantic coast, and probably a long distance into the sea. When the pampas had become thus completely covered, a change occurred once more in the climate; the seasons began to get warmer, and each summer a greater quantity of ice and snow melted than was formed during the winter.

The result of this was that the spring and summer floods increased, and, in place of depositing sand and gravel, they gave rise to huge torrential rivers, with very considerable erosive powers. By the time the ice had all melted away, and the country had settled down once more to a condition of

genial climate, the surface of the land had everywhere been cut into by large river-valleys, with many tributary cañadones. During the genial period which followed the retreat of this great ice-mass, volcanoes began to break out, some pouring out their lava on the surface of the first pampa level, others in the great, broad river-valleys. During all this time the country was slowly rising, and, after a certain interval, which it is impossible at present to determine, the climate once more began to get cold, and the ice began to creep down from the mountains into the plains.

This sequence of events was probably repeated from time to time right through the quaternary era, and, although I have only succeeded in finding four moraines attributable to different horizons, I have reason to believe that the changes mentioned above occurred at least seven times, and in this connexion it is worthy of note, as I will presently explain, that the last moraine found, although of the small valley type, extended practically as far towards the east as the great plateau one first mentioned.

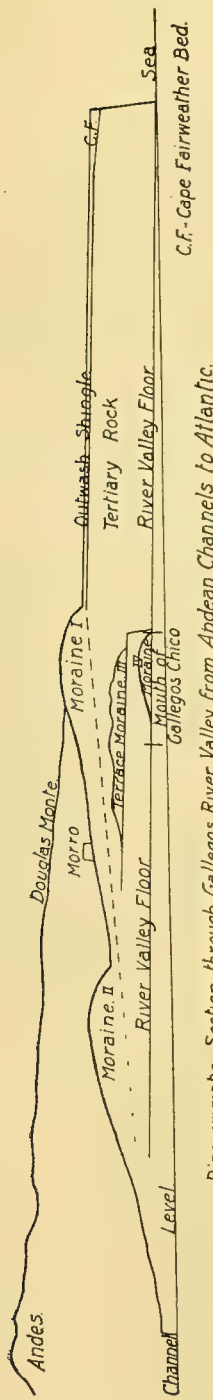
APPENDIX.

On the 28th March, 1915, I left Estancia Alquinta and proceeded to Douglas (Esperanza), on the north side of the Gallegos river, my intention being to study the line of junction between the great terminal moraine and the flat pampa, which I had good reason to believe existed between these two points. After two and a half hours I noticed on going up to the higher level that the pampas had still all the characteristic flatness already described as universally found to the north of the Gallegos river. Here I found myself at the foot of a long, stiff incline, which I ascended, and on the top of which I halted to rest my horse. I here quote from my notes written on the spot:—"28th March. 2 p.m. Rode from Alquinta to Douglas; after entering Bella Vista camp had a long pull up to the top of a pampa. Here the barometer registered five hundred and thirty feet above Alquinta. Could see from this point the change from the flat pampas to the undulatory. There is no very marked rise of level, but the undulatory condition of the surface of the high pampa can be distinctly seen. Mouth of Gallegos Chico from here bore S. by E. magnetic. The pampas have what might be called a drumlin appearance. The line of demarcation between the flat and

undulatory pampas can, on careful observation, be distinctly seen: the difference in level does not at first seem to be more than fifty feet or so, perhaps even less; yet the topography of the two plains is distinct. So far I have not seen an erratic, but hope to see one soon." I restarted along the track, and my next note is as follows: "Had not gone three hundred yards beyond the point where I wrote the above when I came on erratics; not one but several, showing their tops here and there above the ground, several feet in diameter. A little further along they can be seen in all directions; are non-volcanic, and many of them are very large." For about two leagues at least the surface had a tendency to slightly rise, and the rather spread-out drumlin appearance was well marked. About three leagues from the edge of this great moraine is a deep cañadon, running more or less north-west and south-east, with a floor so level that it was very difficult to say which was the direction of its outflow. Its inclination proved to be backwards, away from the valley of the Gallegos. In fact, this cañadon ran into a series of bajos, which eventually, further to the west, discharged themselves into the Gallegos river through a series of cañadones.

Douglas Estancia is situated in a cañadon about thirty feet below the main pampa, about twenty miles to the west of the edge of the terminal moraine. On one or two occasions I carefully estimated its height above the river as about two hundred feet. All the pampas round about the Douglas settlement exhibit a well-marked glacial topography, showing drumlins and erratic blocks everywhere, and consequently these differences in level seemed peculiar. The river runs a very even course from the Douglas camp to the point opposite the end of the terminal moraine below Bella Vista; there are practically no rapids, and the difference in levels in the two localities cannot consequently be more than fifty feet, if so much. This will leave the end of the great moraine about two hundred and eighty feet higher than the plain at Douglas, which is undoubtedly a continuation of the same glacial feature. The particular glaciation which we are now dealing with thus left behind it a large and extensive moraine, at its eastern termination two hundred and eighty feet higher than its level twenty miles further to the west. The topography of this area is rather complicated by the presence of a long narrow ridge which extends out into it from the cordillera in the west; it is about six hundred and fifty feet above the plain at Douglas Estancia, and the ridge is covered by moraine material and shows well-marked drumlins and erratics. It is on an average about a mile or two in breadth, and the fall on the north side is much less than that on the south. I did not estimate its height above the northern plain, but I should judge it to be about one hundred and fifty feet. Now, the tertiary rock underlying the outwash gravel on the flat plain, even close to

the fringe of the moraine, can be seen in places at no great distance, not more than thirty or forty feet, below the surface of the shingle; consequently the surface of the tertiary rock also falls in level as we proceed towards the west, and this fall begins after it becomes overlain by the moraine proper. The accompanying diagram will explain these facts more clearly. Unfortunately, I have never had an opportunity of going further west than the middle of the Douglas land, so I could not study the further topography of this plain in detail; however, from the tops of several high hills I could see in the distance about twenty miles further west than Douglas Estancia another line of high ground as if a second line of terminal moraine similar to that which I have been describing. Intelligent people from whom I have made inquiries have informed me that practically the same sequence of change is found here, namely, a sudden rise of level and a gradual fall, which finally reaches the sea-level at the channels. I have always found that the tertiary rock, even in the middle of the volcanic area, follows a very even course and exhibits very little tendency to dip in any direction, so that I can only conclude that this sloping down to the west is here due to erosion, and that this erosion was of glacier origin. The peculiar sloping erosion of the tertiary rock coincides exactly in extent with the moraine, and we cannot help coming to the conclusion that the same agent operated as a cause in both instances. Once we get well inside the moraine area, we notice that terracing practically disappears from the river valleys. A little below the Bella Vista settlement, at the mouth of the Gallegos Chico, where it joins the Gallegos river, the lower terrace has been cut down by the former river (Gallegos Chico) to the level of the present river valley. This cutting would seem to have belonged to the last erosive phase of the river-valley cutting process, and must have been subsequent to the formation of the moraine-covered terrace further along. Yet down in the mouth of



Diagrammatic Section through Gallegos River Valley from Andean Channels to Atlantic. Four distinct Moraines are shown. That of the Gallegos Chico being the most recent.

the Gallegos Chico, almost filling it from side to side, except where the present river has cut a recent narrow gorge, is found a most perfect little terminal moraine. In Pl. VII, fig. 4, we are looking across the mouth of this valley, and it will be seen that the moraine almost closes it. The present river has cut its way through it, and is running down in a narrow channel a little beyond the horses. I consider this moraine, although very small, most instructive, as it clearly shows that the great erosive action which operated intermittently over an extensive period in the cutting out of the river valleys was accompanied to its termination by the periodic advance of ice in the form of glaciers; and this confirms my already expressed belief that all the terraced river valleys are fluvio-glacial products even down to their lowest levels.

Although I have abundantly looked for it, I have never succeeded in finding anything that would show that during the inter-glacial periods the climate was as genial as at present.

There is everywhere in the country evidence of oscillations of climate, but I have never found any facts which would prove beyond doubt that there was a true inter-glacial epoch. In every terrace I have been able to examine the shingle lies directly on the underlying tertiary rock, and I have never seen any deposit of loam or mud, with animal or plant remains, intervening between them. I have found at least four separate deposits of moraine material, each of them belonging to a different horizon, and probably many more might be found if a systematic search could be made.

The first I found was, as I have already described, the great terminal moraine on the high pampa, from which ran the supra-pampean shingle-layer as an outwash. The second was on a high terrace at the back of Bella Vista, and it was cut into when the river valley was lowered to the next lower level. The third was an extensive terminal moraine about fifteen miles to the west of Douglas Estancia. Finally, I found, as mentioned above, a very well-marked small terminal moraine filling the mouth of the Gallegos Chico river valley, where it opens into the Gallegos river, and having its base almost on the present level of the latter. Now, the Gallegos Chico valley is cut down through over two hundred feet of Buitreras bed, which, we have already seen, was probably formed on the floor of an inter-glacial lake. This shows that at the very end of the river-valley period, when their beds had been lowered to their present levels, tongues of glacier extended into the river valleys as far to the east as the first great plateau glacier which gave origin to the pampa shingle.

The diagrammatic section through this portion of Patagonia from west to east shows the position of these four moraines.

55°
75°
74°
73°
72°
ATLANTIC

Lago San Martin
Lago Viedma
Lago Argentino
Basalt
Rio Santa Cruz
San Julian
SANTA CRUZ
3rd Pampa
Old Coast Line
2nd Pampa
Old Coast Line
Coy Inlet
Rio Coyle
Pampa
Pampa
Pampa
L. Sarmiento
Lago Del. Toro
LIMIT OF FIRST ICE
Ultima Esperanza
Douglas Monte
Bella Vista
Pampa Alta
Pampa Rio
Bulferos
Quer Aike
Tillit Aike
Bahia Gallegos
Gallegos Chico
C. FAIRWEATHER
Punta Loyola
Old Coast Line
Paciake
North Hills
Frailes
Three Brothers
Cerra Diablo
Mt AYMONT
ADVANCE
Gallegos Chico
C. VIRGENES
C. DUNGENESS
MAGELLANES STRAITS
La Blanca
OTWAY
PUNTA ARENAS
SAN SEBASTIAN
OCEANO PACIFICO
OCEANO ATLANTICO
TIERRA DEL FUEGO
Lago. Fagnano
49°
50°
51°
52°
53°
54°
55°
74°
73°
72°
71°
70°
69°
68°
67°
66°
65°
75°

FIGURE 1.

FIGURE 2.

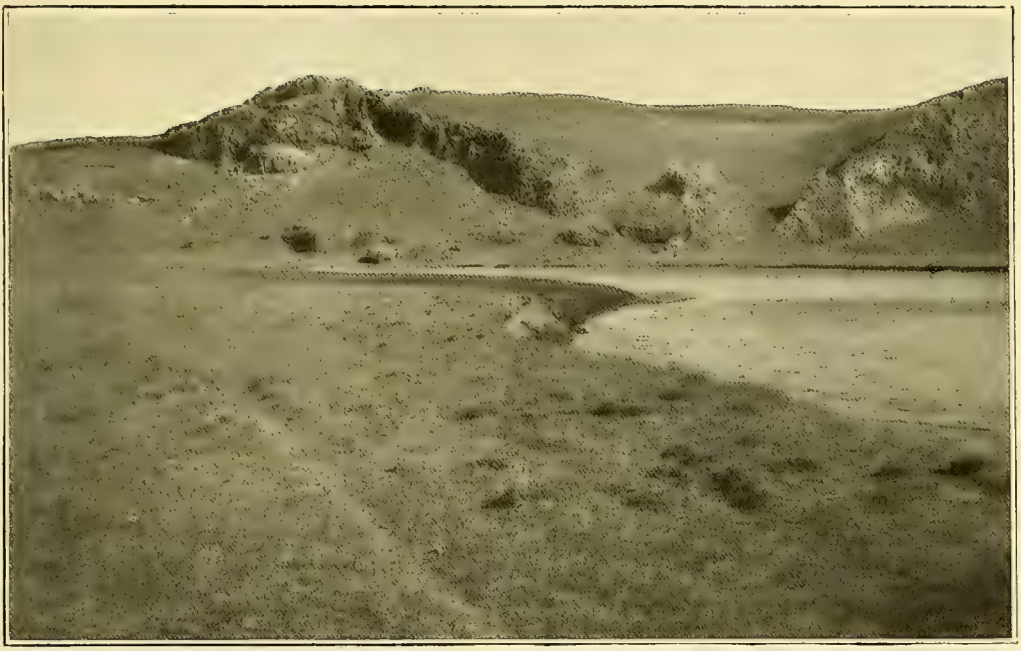


FIGURE 3.

FIGURE 4.

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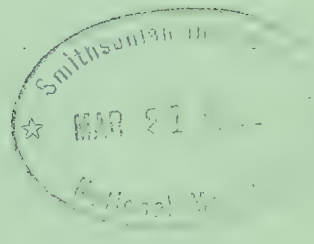
AWARD OF THE BOYLE MEDAL

TO

GEORGE H. PETHYBRIDGE, B.Sc., Ph.D.

1921



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In conclusion, I wish to tender my most sincere thanks to Professor Cole for the encouragement he has always given me, and the kind interest he has taken in my studies from the beginning. He first taught me to take an interest in geological matters, and has very kindly read over the present paper, and given me many valuable suggestions on the interpretation of the facts observed.

EXPLANATION OF PLATES.

PLATE V.—Map.

PLATE VI.

Fig.

1. View of portion of the pampa extending inland from the Atlantic coast north of Cape Fairweather.

2. Sloping blocks of basic lava, wind-worn and grooved, sloping upwards towards the east.

PLATE VII.

3. Buitreras cone, 300 feet high. It is cut through the centre of the crater. One-half swept clean away by the river.

4. Gallegos Chico moraine, filling the mouth of the Gallegos Chico river-valley, where it joins the main river.

XX.

AWARD OF THE BOYLE MEDAL

TO GEORGE H. PETHYBRIDGE, B.Sc., Ph.D.

1921.[1]

In submitting the name of Dr. George H. Pethybridge as that of a suitable recipient for the Boyle Medal, the Science Committee have specially in mind his important work in connexion with the elucidation of the life-history of the fungus which causes the potato blight.

There are, perhaps, few subjects in plant pathology to which so much attention has been devoted as to the potato blight. Research in this field is attractive, not only from a scientific standpoint, but also from a practical and economic point of view. Since its first appearance in the middle of last century, a very considerable mass of literature concerned with this disease has accumulated, emanating from investigators in the laboratories of purely scientific institutions, agricultural stations, and elsewhere. Thus most of the simpler and more obvious features concerning the disease and its causative parasite had been made thoroughly clear long ago, leaving for the new-comer only the more baffling problems to be attacked and solved.

The fungus itself which causes the potato blight has long been known, and the work of the earlier observers was critically summarized and substantially added to by the important and authoritative researches of de Bary, culminating in 1876. A vegetative or asexual stage only was known with certainty at that time, and it is during this stage that the parasite plays such havoc amongst the potato plants during the summer, often utterly destroying the foliage and seriously reducing the yield of tubers. Furthermore, it was known that infection spreads from the green parts of the plants above ground, reaches the tubers, and causes them to decay and become practically useless. Exactly how the fungus in the first instance reached the foliage was a problem upon which the investigators of the day were by no means agreed.

Several closely allied fungi were known which, in addition to possessing a vegetative stage, also produced sexual organs during, or towards the end of,

[1] The presentation was made at the Scientific Meeting of the Royal Dublin Society, held on February 22, 1921.

the parasite's active season. As the result of the interaction of these organs, globular reproductive bodies—*oospores*—are formed. Having hard, thick, protective coats, these oospores lie dormant for a time, but when suitable conditions supervene they germinate and produce new parasites.

In the case of *Phytophthora infestans* such oospores had not been discovered. True, there were one or two investigators who claimed to have found them, and who maintained that the parasites developing from them were responsible for the infection of the crop in the succeeding year. Nevertheless, the critical studies of de Bary, alluded to above, show that these claims were not substantiated.

The investigations of Dr. Pethybridge and others have been so complete that it is now practically certain that no such infection by means of oospores takes place. These bodies have never really been found in the tuber or in any other part of the plant, in spite of most careful and prolonged search. If they ever are formed there, their formation is so rare that it cannot be of any importance as a source of infection of the crop.

Seeing that re-infection of the crop is not provided for by the production of oospores, it was maintained that the mycelium of the parasite grew down from the leaves, reached the tubers through the aerial and underground stems, became dormant there as the tubers matured, and remained in this condition throughout the winter. In the following season, when the "seed" potatoes began to sprout, it was believed that this mycelium, till then supposedly dormant in the tubers, woke up, and, keeping pace with the growing stems and leaves, entered the latter, and remained there in a quiescent state, until the warm weather of the summer started it into activity and destructiveness.

Despite the most painstaking microscopic investigations, these invading and temporarily innocuous mycelia were never discovered; and all the observations and experiments directed towards solving the question showed that the well-known and easily visible spots of blight on the foliage—up to that time usually regarded as the earliest stages of a fresh outbreak—were the result of infection by air-borne spores.

By experiments carried out over several years, Dr. Pethybridge has contributed important evidence supporting this latter view. Furthermore, his experimental work in greenhouse and garden (supplemented later by that of other workers under field conditions) has revealed that there is a still earlier phase, rarely to be met with and easily overlooked, in which the fungus (by no means in a dormant condition) does invade certain sprouts which, if not all too quickly killed, may succeed in getting above ground. It is now generally accepted that it is from aerial spores produced by the

fungus living in such shoots that the infection is derived which, under suitable weather conditions, develops into an epidemic.

During his investigations of the various diseases of the potato, Dr. Pethybridge succeeded in detecting at least one new parasite, and in adding considerably to our knowledge of several others which contribute to the losses sustained by this important crop. The new (and by far the most important) one was named *Phytophthora erythroseptica*. Not only does this parasite cause great losses—sometimes greater even than those caused by *P. infestans*, and hence the importance of its discovery from a practical point of view—but also its discovery and investigation have contributed fundamentally to our knowledge of *P. infestans*, and has brought to light a method of development of sexual organs which up to that time was quite unique in the vegetable world.

De Bary has described the fertilization of certain fungi related to the Phytophthoras. In these the female germ-plasm is contained in a globular capsule, the oogonium. Close to this there arises a club-shaped capsule, the antheridium, containing the male germ-plasm. A beak is formed on the antheridium which applies itself to the oogonium and penetrates it. Through this beak the male germ-plasm passes into the female germ-plasm, and so effects fertilization. This process is known in several parasites described as species of Phytophthora, and no one doubted that the same process would be found to take place in *P. infestans* if and when the sexual organs of this species were discovered.

It was, therefore, with no little surprise that Dr. Pethybridge found in his cultures of *P. erythroseptica* that the developing oogonia *grow through* the young antheridia, and that the oospore is formed in the oogonium after its emergence on the far side of the antheridium. Such a penetration of the male organ by the female had till then been quite unknown.

Having established this peculiar and novel type of development for what we may call Dr. Pethybridge's fungus, he next turned his attention to the origin of the oospore in *P. infestans*. For it must be stated now that meanwhile in the United States of America, Dr. Clinton had succeeded in forcing this parasite to produce sexual organs, not, indeed, in any part of the living potato plant, but as a saprophyte in pure culture *in vitro*. Dr. Pethybridge, with his assistant, Mr. P. A. Murphy, using a slight modification of Clinton's medium, succeeded in confirming the fact of oospore formation in *P. infestans*, but was able to show in addition the important fact that the method of development followed was not that which had been expected, but was identical with the one which he had just previously discovered in *P. erythroseptica*. Since then, in Dr. Pethybridge's laboratory,

a third *Phytophthora* of this type has been discovered,[1] and work is now in progress there on still another species, in which both modes of development obtain in one and the same individual.

It may be mentioned that within the last couple of years Mr. P. A. Murphy has placed the coping stone on Dr. Pethybridge's work by describing the cytological details of this most interesting method of fertilization.

Dr. Pethybridge has also carried out other important researches, chiefly connected with plant pathology. The results of many of these, like those on the potato blight, have been communicated to and published by the Royal Dublin Society. Although from the scientific point of view none of these investigations is so unique and so unexpected in its outcome as that on the potato blight, yet they have yielded important results, increasing and consolidating our knowledge of obscure forms of life, and providing a foundation from which future methods of practical control may be elaborated.

Looking at Dr. Pethybridge's work from another point of view, it is proper to record here that as Economic Botanist and Head of the Seeds and Plant Disease Division of the Department of Agriculture and Technical Instruction for Ireland, he has been responsible for its organization and for direction of research in vegetable pathology.

His work has not been carried out solely within the permanent laboratories at headquarters. He has introduced an important innovation by having field laboratories established in the actual areas where the particular diseases under investigation are most prevalent. There the worker can be in the closest possible contact with his patients during practically the whole period of development. It was in these laboratories that most of Dr. Pethybridge's researches, including that on the potato blight, were carried out.

Owing to Dr. Pethybridge's initiative, the study of plant diseases in this country has been greatly stimulated, and, as a result of his scientific spirit, the same degree of thoroughness and rigorous experimental technique is being applied to their investigation as it is customary to expect when diseases of man and of animals are being studied. Thus it is fair to say that the science of Phytopathology has benefited from his work not only through his actual contributions to knowledge, but also by his example in discarding merely observational and descriptive methods of work, and in substituting for them experimental methods of the most exact description.

A list of Dr. Pethybridge's chief published contributions to science is appended.

---

[1] Other species have also been described in India and America.

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1. The Leaf-Spots of *Arum maculatum.* Irish Naturalist, xii, 6, p. 145. 1903.
2. An improved simple form of Potometer. Sci. Proc. Royal Dublin Society, x (N.S.). 16, p. 149. 1904.
3. The Vegetation of the District lying South of Dublin (with map). Proc. Royal Irish Academy, xxv, B. 6, p. 124. 1905. *With R. Ll. Praeger.*
4. The Causes of "Blowing" in Tins of Condensed Milk. Econ. Proc. Royal Dublin Society, i, 7, p. 306. 1906.
5. Report on Tests made with the new French Potato *Solanum Commersonii* Violet, and the "Blue Giant." Journ. Dept. Agric. and Tech. Inst., Ireland, viii, 2, p. 247. 1908.
6. Dry Rot of the Potato Tuber. Econ. Proc. Royal Dublin Society, i, 14, p. 547. 1908. *With E. H. Bowers.*
7. Potato Diseases in Ireland. Journ. Dept. Agric. and Tech. Inst., Ireland, x, 2, p. 241. 1910.
8. A Census Catalogue of Irish Fungi. Proc. Royal Irish Academy, xxviii, B. 4, p. 120. 1910. *With J. Adams.*
9. A bacterial Disease of the Potato Plant in Ireland. *Ib.*, xxix, B. 1, p. 1. 1911. *With P. A. Murphy.*
10. Considerations and Experiments on the Supposed Infection of the Potato Crop with the Blight Fungus (*Phytophthora infestans*) by means of Mycelium derived directly from the planted Tubers. Sci. Proc. Royal Dublin Society, xii (N.S.), 2, p. 12. 1911.
11. Investigations on Potato Diseases (Second Report). Journ. Dept. Agric. and Tech. Inst., Ireland, xi, 3, p. 417. 1911.
12. The "Bladder Rust" of Scots Pine. *Ib.*, p. 500.
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14. The Methods employed in testing Grass Seeds. Journ. Econ. Biology, vii, 2, p. 41. 1912.
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16. Investigations on Potato Diseases (Fourth Report). Journ. Dept. Agric. and Tech. Inst., Ireland, xiii, 3, p. 445. 1913.

17. On the Rotting of Potato Tubers by a new species of Phytophthora having a method of Sexual Reproduction hitherto undescribed. Sci. Proc. Royal Dublin Society, xiii (N.S.), 35, p. 529. 1913.

18. On Pure Cultures of *Phytophthora infestans* de Bary and the Development of Oospores. *Ib.*, 36, p. 566. 1913. *With P. A. Murphy.*

19. Further Observations on *Phytophthora erythroseptica* Pethyb., and on the Disease produced by it in the Potato Plant. *Ib.*, xiv (N.S.), 10, p. 179. 1914.

20. Investigations on Potato Diseases. (Fifth Report.) Journ. Dept. Agric. and Tech. Inst., Ireland, xiv, 3, p. 433. 1914.

21. Recent Advances in our Knowledge of the genus Phytophthora. Journ. Econ. Biology, ix, 2, p. 53. 1914.

22. The Spread of the Celery Leaf-Spot Disease by the use of Affected Seed and its Prevention. Journ. Dept. Agric. and Tech. Inst., Ireland, xiv, 4, p. 687. 1914.

23. Investigations on Potato Diseases. (Sixth Report.) Journ. Dept. Agric. and Tech. Inst., Ireland, xv, 3, p. 491. 1915.

24. Cultivation of Seaweed in Ireland. Journ. Dept. Agric. and Tech. Inst., Ireland. *Ib.*, p. 546.

25. The possible Source of Origin of the Leaf-Spot Disease of cultivated Celery. Journ. Roy. Hort. Soc., xl, 3, p. 476. 1915.

26. The Verticillium Disease of the Potato. Sci. Proc. Royal Dublin Society, xv (N.S.), 7, p. 63. 1916.

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28. Further Observations on the cause of the common Dry-Rot of the Potato Tuber in the British Isles. Sci. Proc. Royal Dublin Society, xv (N.S.), 21, p. 193. 1917. *With H. A. Lafferty.*

29. Investigations on Potato Diseases. (Eighth Report.) Journ. Dept. Agric. and Tech. Inst., Ireland, xvii, 4, p. 595. 1917.

30. A Disease of Flax Seedlings caused by a Species of Colletotrichum, and transmitted by infected seed. Sci. Proc. Royal Dublin Society, xv (N.S.), 30, p. 359. 1918. *With H. A. Lafferty.*

31. Investigations on Potato Diseases. (Ninth Report.) Journ. Dept. Agric. and Tech. Inst., Ireland, xviii, p. 410. 1918.

32. A Disease of Tomato and other Plants caused by a new species of Phytophthora. Sci. Proc. Royal Dublin Society, xv (N.S.), 35, p. 487. 1919. *With H. A. Lafferty.*

33. Heterocarpy in *Picris echioides*. Irish Naturalist, xxviii, 3, p. 25. 1919.

34. Investigations on Potato Diseases. (Tenth Report.) Journ. Dept. Agric. and Tech. Inst., Ireland, xix, 3, p. 271.

35. A destructive Disease of Seedling Trees of *Thuja gigantea* Nutt. Quart. Journ. Forestry, xiii, 2, p. 93. 1919.

36. Is it possible to distinguish the Seeds of Wild White Clover from those of Ordinary White Clover by Chemical Means during a Germination Test? Econ. Proc. Royal Dublin Society, ii, 14, p. 248. 1919.

37. Notes on some saprophytic species of Fungi, associated with diseased Potato Plants and Tubers. Trans. British Mycol. Soc., vi, 2, p. 104. 1919.

38. Investigations on Flax Diseases. Journ. Dept. Agric. and Tech. Inst., Ireland, xx, 3, p. 325. 1920. *With H. A. Lafferty.*

SCIENTIFIC PROCEEDINGS.

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SCIENTIFIC PROCEEDINGS

OF THE

ROYAL DUBLIN SOCIETY.

Vol. XVI. (N.S.), Nos. 21–24. AUGUST, 1921.

21.—THE CONCENTRATION AND PURIFICATION OF ALCOHOLIC FERMENTATION LIQUORS. PART I.—THE DISTILLATION IN STEAM OF CERTAIN ALCOHOLS. By JOSEPH REILLY, M.A., D.Sc., M.R.I.A., F.I.C., and WILFRED J. HICKINBOTTOM, M.Sc., A.I.C.

22.—THE "BROWNING" AND "STEM-BREAK" DISEASE OF CULTIVATED FLAX (*LINUM USITATISSIMUM*), CAUSED BY *POLYSPORA LINI* n. gen. et sp. By H. A. LAFFERTY, A.R.C.Sc.I., Assistant in the Seeds and Plant Disease Division, Department of Agriculture and Technical Instruction for Ireland. [Communicated by Dr. George H. Pethybridge, B.Sc.] (Plates VIII–X.)

23.—A NEW PRINCIPLE IN BLOWPIPE CONSTRUCTION. By H. G. BECKER, A.R.C.Sc.I., A.I.C., Demonstrator in the Royal College of Science, Dublin.

24.—UNCHARGED NUCLEI PRODUCED IN MOIST AIR BY ULTRA-VIOLET LIGHT AND OTHER SOURCES. By the late PROFESSOR J. A. MCCLELLAND, F.R.S., and J. J. M'HENRY, M.Sc., University College, Dublin.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XXI.

THE CONCENTRATION AND PURIFICATION OF ALCOHOLIC FERMENTATION LIQUORS.

Part I.—The Distillation in Steam of Certain Alcohols.

By JOSEPH REILLY, M.A., D.Sc., M.R.I.A., F.I.C.,
AND
WILFRED J. HICKINBOTTOM, M.Sc., A.I.C.

[Read January 25. Published August 19, 1921.]

The monohydric aliphatic alcohols may be considered as being formed from water by the substitution of an alkyl group for one of the hydrogen atoms. They may also be regarded as hydroxyl derivatives of the saturated paraffins. From the former standpoint the water-alcohol mixtures would be of the type of *closely-related* liquids. According to the latter view, while paraffin-alcohol mixtures would conform to this type, aqueous alcohol compositions would more readily be classified among mixtures of *not-closely-related* liquids. From both these aspects the subject has been studied by Young[1] in his investigation of the relationship of the alcohols to water on the one hand, and to the paraffins on the other. In general the influence of the alkyl group rapidly increases as we pass from methyl alcohol up the series. Furthermore, from the study of the vapour pressures of various mixtures of alcohols and water,[2] it has been shown that the relation between the molecular percentage of methyl alcohol in the mixture and the corresponding vapour pressure may be represented by an approximately straight line. Comparisons were made by Young from Konowalow's data at such a temperature that the vapour pressure of the pure alcohol in each case was 400 mm. With the substitution of ethyl alcohol for methyl alcohol in the above comparison, the relation is represented by a decided curve. In the case of the higher alcohols the curve becomes still more pronounced.

It would, therefore, appear that methyl alcohol water mixtures come into the group of *closely-related* miscible liquids, while ethyl alcohol and water mixture is better classified with the miscible *not-closely-related* mixtures.

[1] Trans. Chem, Soc., 1902, 81, 707. [2] Konowalow, Weid. Ann., 1881, 14, 34.

In the case of some of the higher alcohols obtained by fermentation, such as *iso*-butyl and *iso*-amyl alcohols, only partly miscible mixtures are obtained with water, and it is more convenient to classify these as *partly miscible, not-closely-related,* mixtures.

Investigations on the distillation of homogeneous mixtures were first carried out by Gay-Lussac,[1] and subsequently by Magnus,[2] Regnault,[3] Berthelot,[4] and others. This early work was correlated by Duclaux, who used it as the basis of experimental work, which led to the establishment of a relation between the composition of the liquid to be distilled and the distillate. He states[5] that ethyl alcohol distils from aqueous solution more slowly than amyl or *iso*-butyl alcohols.

One of the processes adopted for the purification of ethyl alcohol on a technical scale consists in the distillation of a dilute aqueous solution of the "raw spirit."[6] Under these conditions the fusel oil, various esters, and other impurities are removed more readily than the ethyl alcohol, and in consequence are collected in the first running. The dilute solution of ethyl alcohol collected in the subsequent fractions is then concentrated. The process depends on the fact that the higher alcohols distil from dilute aqueous solution at a more rapid rate than does ethyl alcohol.

Duclaux studied the rate of distillation of the alcohols with diminishing volume. He took a certain volume of aqueous alcohol and distilled it, collecting the distillate in several fractions. By expressing the volume of the alcohol as a percentage of the total amount distilled he obtained a series of constants for each alcohol which served to identify the particular alcohol.

As the original method outlined by Duclaux does not give concordant results with different workers, a large amount of experimental work has been carried out to remedy the discrepancies observed. It has been shown that the loss of heat from the exposed flask and still-head, by convection currents and radiation, leads to irregular results. Various arrangements for preventing this have been used. It is not, however, advisable to keep the exposed flask at a higher temperature than that of the vapour, otherwise errors will be introduced by splashing and by complete evaporation of drops of solution. The best conditions for preventing condensation are obtained by surrounding the flask with a steam jacket.

The original formula of Duclaux may be expressed thus :—

$$\frac{da}{db} = c\frac{a}{a+b},$$

[1] Ann. de Physique et de Chimie, 1815.
[2] Ann. de Physique et de Chimie, 1836.
[3] Phil. Mag., 1855, 9, 4.
[4] Comptes rendus, 1863, 57, 430, 985.
[5] Ann. inst. Past., 1895, ix, 575.
[6] E. Guillaume, E.P., 5194, 1902.

where a and b represent the percentage by volume of alcohol and water respectively in the original liquid, and da and db the percentage of alcohol and water respectively in the vapour. The above relation may be represented by a hyperbola. The value for c with dilute solutions of various alcohols varies from 10·9 for methyl alcohol to 50 for amyl alcohol and 61 for capryl alcohol. The coefficient c increases with the molecular weight of the alcohol. The relation established by Duclaux has been verified for ethyl alcohol and several of the higher alcohols up to the point corresponding with mixtures of constant boiling point.

Sorel,[1] pursuing the problem from the point of view of its industrial application, carried out distillations on quantities of four litres of liquid. He took precautions to prevent loss of heat by radiation, and probably it is due to this fact that his results differ somewhat from those of Duclaux. Against the volume distilled, Sorel plotted the composition of the remaining liquid, and obtained a curve representing the rate of elimination of alcohol from the aqueous solution.

The distillation of dilute solutions can be represented approximately by the expression

$$Va = (V - dV)(a - da) + U dV,$$

or

$$U = a + V\frac{da}{dV},$$

where

V = volume remaining in the flask at any moment;
a = concentration of alcohol in the solution;
U = concentration of alcohol in the distillate.

Mariller[2] uses the coefficient K, which is given by

$$K = \frac{\text{percentage of alcohol in vapour}}{\text{percentage of alcohol in liquid}},$$

or, in the Duclaux notation (see above), $= \frac{da}{a} = \frac{100\,c}{ac + 100}$.

It is found that the coefficient K, which may be called the coefficient of solution, or better, the coefficient of enrichment, is dependent on the alcoholic concentration. It is found that on Sorel's formula, $K = 9{\cdot}9$ for ethyl alcohol of 1 per cent. concentration, and this value gradually diminishes as a increases. With $a = 20$ $K = 3{\cdot}31$, with $a = 50$ $K = 1{\cdot}5$, and, as a increases, the value of K gradually falls from 1·5 to 1. Thus for $a = 96$, $K = 1{\cdot}002$, and for $a = 97$, K is recorded as 1·001, and for $a = 100$, K is given as 1. The last two values are apparently incorrect, for it would be expected that K should

[1] Comptes rendus, 1892, **116**, 693.

[2] "La Distillation Fractionnée," 1917, p. 23: cf. also "Le Bulletin de l'Assoc. des Chimistes," 1911, p. 473, &c.; and "La Distillation," p. 147.

equal unity for a concentration of 95·47, while for higher concentrations K should fall to less than unity.

From the industrial point of view it is necessary to know, during the purification of the alcohols, the rate at which the impurities are removed with respect to the ethyl alcohol.

If s be the weight of impurities in part of kilogram per kilogram of the original liquid, and S the weight of impurities in 1 kilogram of the mixed vapour, Sorel gives the following relationship:

$$S = K_1 s + K_2 s^2 + K_3 s^3 \ldots .;$$

or

$$S = K_1 s \text{ approximately.}$$

The distillation of mixtures of ethyl alcohol, higher alcohols, various esters, aldehydes, &c., and water over a wide range of alcohol concentration has been made by Barbet.[1]

The ratio

$$\frac{\text{Percentage of "impurities" in ethyl alcohol in distillate}}{\text{Percentage of "impurities" in ethyl alcohol in liquid}}$$

he designated by K', and it is known as the coefficient of purification. If

$$k' = \frac{\text{percentage by wt. of impurities (i.e. amyl alcohol, &c.) in vapour}}{\text{percentage by wt. of impurities (amyl alcohol, &c.) in liquid}},$$

then $K' = \dfrac{k'}{K}$.

The value for K' is dependent largely on the alcoholic concentration of the solution. It indicates how far distillation will remove this impurity from the alcohol, apart altogether from the quantity of water present. This "coefficient of purification" is of more technical value than the coefficient of enrichment.

Using a similar notation to that employed by the authors in the study of the fatty acids,[2] the K of Sorel may be expressed in a slightly different form where

a = initial amount of alcohol in flask;

x = amount of alcohol in distillate after volume v has distilled

V = constant volume of liquid in flask.

If ρ = density of water vapour in the flask, and σ = weight of water per unit volume of distillate, we have

$$K = \frac{\text{concentration in vapour phase} \times \sigma}{\text{concentration in liquid phase} \times \rho}$$

$$= k\frac{\sigma}{\rho}, \qquad \lambda = k\frac{\sigma}{\rho V},$$

$$= \lambda V \text{ or } A \times V \times 2{\cdot}3026, \quad \text{where } A = \frac{1}{v}\log\frac{a}{a-x}.$$

[1] "La Rectification et les colonnes Rectificatrices," 1895, p. 46.

[2] Sci. Proc. R.D.S., 1919, xv, 519.

Using this expression, the values of the coefficient of Sorel corresponding to those of $\frac{1}{v} \log \frac{a}{a-x}$ have been calculated for solutions of alcohol of different concentrations (see later).

The distillation coefficients of the alcohol change with the concentration. Only a few results are given showing the change of constant with concentration; but these confirm the results of Sorel and Gröning. With dilute solutions of the acids the alteration in the rate of distillation from an aqueous solution can be satisfactorily explained by taking into consideration the degree of ionic dissociation. For the alcohols this explanation cannot apply. The alcoholic solutions are generally more concentrated than those employed in investigations on the acids, consequently the temperature of the aqueous solution may be a determining factor. Another possible disturbing effect may be due to the association of the alcohol. Murray[1] has adduced evidence that the molecules which are usually associated in the liquid state are generally not associated in aqueous solution. If there still exist in the solution some associated molecules at the concentration employed, there will be a continual change in the state of molecular aggregation as the distillation proceeds. Under these conditions Nernst's law of distribution will not hold, consequently the distillation coefficient may vary.

As a general rule, the application of Nernst's law to the distillation of solutions furnishes us with a method of determining whether a substance behaves normally in solution. Water has been used in all the investigations, chiefly on account of the convenience. Other solvents, such as alcohols, amines, or any other substance which is sufficiently volatile to carry over the solute in the vapour may also be employed.

In the experiments on the distillation of alcohol-water mixtures referred to, the distillations have all been carried out at varying volumes. In the present paper, however, the authors have investigated the distillation coefficients of methyl, ethyl, *n*-propyl, *n*-butyl, *iso*-butyl, *sec*-butyl, and *iso*-amyl alcohols obtained by distilling constant volumes of dilute aqueous solutions of the alcohols.

Method of Distillation employed.

The distillation of dilute solutions of the lower alcohols was carried out at constant volume in a similar type of apparatus to that employed by us for the distillation of the fatty acids. 200 c.c. of a dilute aqueous solution of an alcohol were distilled, and the volume of liquid in the flask kept constant

[1] Amer. Chem. Jour., 1903, **30**, 193.

throughout the experiment by adding water at the same rate as the solution distilled over. The distillate was collected in approximately equal fractions of 5 or 10 grams. The distillation was carried out at the approximate rate of 60 c.c. per hour. It was found convenient to employ a set of receivers, which were weighed and provided with stoppers. Before a distillation the cylinders were thoroughly cleaned with a solution of chromic acid in concentrated sulphuric acid, and finally washed several times with distilled water. They were then drained by inverting them in a clean beaker. Immediately after a fraction had been collected, the cylinder was removed and stoppered until a determination of the alcohol could be carried out.

The Alcohols investigated.

The alcohols were carefully purified by repeated fractionation, and usually a fraction boiling within 0·2° was reserved.

Methyl Alcohol was obtained from the purest commercial methyl alcohol free from acetone and ethyl alcohol. A sample was collected after two fractionations from an eight-section "Young evaporator fractionating column." It boiled at 64·4–64·6° at 759 mm. pressure. Density = 0·7965 at 15·5/15·5°.

Ethyl Alcohol was purified by refluxing over solid potassium hydroxide, then over freshly ignited quicklime, and finally over calcium. On fractionation the alcohol was obtained of density 0·7937 at 15·5/15·5° and boiling at 78·3–78·4°/761 mm.

n-Propyl Alcohol was obtained from fusel oil by repeated fractionation. The distillate collected between 97 and 97·5° 760 mm. was reserved for the determination of the distillation constant. Although a considerable quantity of fusel oil was fractionated, using both a Young column and a long fractionating column with Lessing rings (copper), only a very small proportion of alcohol with a boiling point 97·2/763 mm. and density 0·8078 at 15·5/15·5° was obtained. The purity of this alcohol is probably not of the same order as in the case of the other alcohols examined.

n-Butyl Alcohol was obtained by fermentation, and after drying it thoroughly over quicklime and potassium carbonate, it was fractionally distilled several times—until the density showed no alteration on further treatment. Boiling point = 117·6°/760 mm.; density = 0·8137 at 15·5/15·5°.

sec-Butyl Alcohol was obtained from *n*-butyl alcohol. The normal alcohol was converted into β-butylene, which was absorbed by moderately concentrated sulphuric acid under pressure yielding *sec*-butyl hydrogen sulphate. The alcohol was obtained by hydrolysis, and was purified by drying and

repeated distillation. Boiling point, 99·4–99·5°/755 mm. and density 0·8114 at 15·5/15°.

iso-Butyl and iso-Amyl Alcohols were purified by repeated fractionation of the purest commercial alcohols obtainable. The *iso*-butyl alcohol had a boiling point of 107·8°/758 mm., and density 0·8063 at 15·5/15·5°, while the *iso*-amyl alcohol boiled at 130·5°–131·5°/757 mm., and had a density of 0·8158 at 15·5/15·5°.

Estimation of the Alcohols in the distillate.

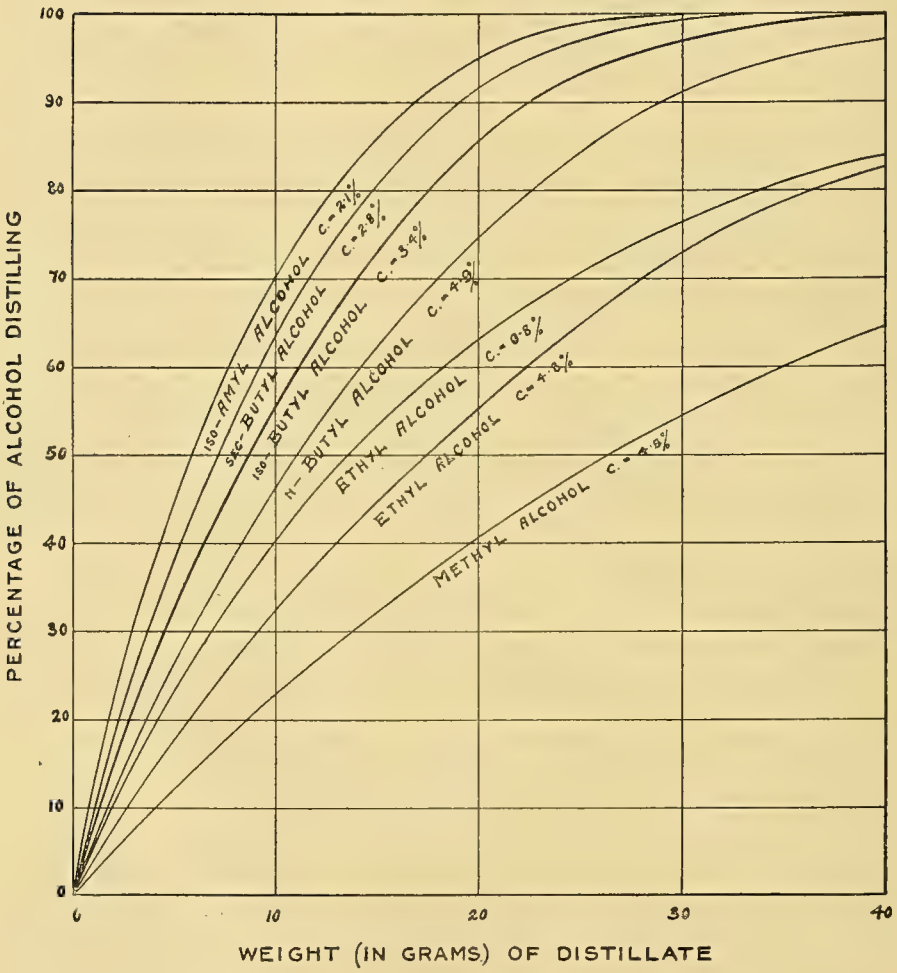
The alcohol in the distillate was estimated by two methods—(*a*) by density, using Perkin's modified arrangement of the pyknometer suggested by Sprengel, and calculation from density tables of alcohol and water mixtures; (*b*) by oxidation, the method of Benedict being employed. In the oxidation method the analysis was carried out as follows. To a known volume (2 c.c.) of the alcoholic distillate, which had been suitably diluted, 20 c.c. of a standard solution of potassium dichromate in sulphuric acid solution was added cautiously. It was found advisable to cool the alcoholic solution during the addition of the chromic acid solution. The oxidation was completed by heating the mixture on a vigorously boiling water bath for five minutes. After diluting the acid-oxidation mixture, ferrous ammonium sulphate was added, and the excess of the latter determined by titration with standard dichromate. The difference in the volume of the dichromate used for the blank experiment and the actual determination is a measure of the alcoholic content of the solution. A factor for converting c.c. of dichromate into weight of alcohol had to be determined for each alcohol by preparing solutions of known concentration. It was found that the constants for the primary alcohols, excluding methyl alcohol, were proportioned to the molecular weights. This indicates that the oxidation of these alcohols probably proceeds with the formation of the corresponding acid.

In the treatment of the *n*-butyl alcohol with the dichromate reagent, an odour resembling that of an ester was observed. By using an insufficiency of the oxidising agent, the odour became more pronounced, due evidently to greater formation of the ester. This reaction between *n*-butyl alcohol and potassium dichromate and sulphuric acid was studied in some detail (see later). When the alcohols were only partially soluble in water, a determination of the volumes of each layer was used as an alternative method in determining the alcoholic content of the distillate. In the case of *n*-butyl alcohol, by the use of the *n*-butyl alcohol-water density curve already prepared

by one of the authors,[1] it was possible to estimate the alcohol after definite dilution.

Rates of Distillation

The experimental results are given in Tables I and II, while the percentage of alcohol distilling in each fraction is shown graphically in the figure.



[1] Sci. Proc. R.D.S., 1919, xv, 43, 598.

Table I.

Alcohol. Initial volume = 200 c.c.	Concentration in grams of Solute per 100 c.c.	Weight of Distillate.	Percentage of Alcohol collected in Distillate.	$\frac{1}{v}\log\frac{a}{a-x}$
Methyl,	4·5	10·14	23·2	0·0113
	,,	20·01	40·5	0·0113
	,,	29·97	55·1	0·0116
	,,	50·53	72·8	0·0112
Ethyl,	0·81	10·52	41·7	0·0222
	,,	21·17	64·4	0·0211
	,,	31·38	77·3	0·0205
	,,	41·74	84·0	0·0191
	,,	52·22	88·4	0·0179
Ethyl,	4·81	9·71	32·1	0·0173
	,,	19·51	55·1	0·0178
	,,	29·65	72·2	0·0187
	,,	39·39	82·2	0·0190
	,,	49·31	88·1	0·0187
	,,	59·29	91·0	0·0176

Table II.

Alcohol. Initial volume = 200 c.c.	Concentration in grams of Solute per 100 c.c.	$\frac{1}{v}\log\frac{a}{a-x}$
Propyl,	2·5	0·026
n-Butyl,	4·9	0·030
iso-Butyl,	3·4	0·047
sec-Butyl,	2·8	0·050
iso-Amyl,	2·1	0·053

The distillation coefficient $\frac{1}{v}\log\frac{a}{a-x}$, as previously shown, is equal to $\frac{k\sigma}{\rho V}$, and on the assumption that $\frac{\sigma}{\rho}$ is constant, the coefficient varies as $\frac{k}{V}$,

and is, therefore, inversely proportional to the initial volume of liquid distilled. The distillation coefficient varies (but to a less extent) with the concentration, and, therefore, in indicating the values of $\frac{1}{v} \log \frac{a}{a-x}$, it is necessary to specify the initial volume distilled and also the concentration. The values recorded in Tables I and II have initial volumes of 200 c.c., this volume having been found to be a convenient one to work with in the case of the alcohols. As, however, in the work on the fatty acids volumes of 150 c.c., were employed, the values of the coefficient obtained on the distillation of 150 c.c. of the alcohols are given in Table III for comparison.

TABLE III.

Alcohol (V = 150 c.c.)	$\frac{1}{v} \log \frac{a}{a-x}$	Concentration.
Methyl, .	0·015	4·3
Ethyl, .	0·024	4·7
n-Butyl, .	0·040	4·8
iso-Butyl, .	0·066	2·9
sec-Butyl, .	0·066	2·8
iso-Amyl, .	0·072	2·1

Even with the variation in concentration, it will be seen that the results of the two series of experiments at 150 c.c. and 200 c.c. initial volume, confirm that the distillation figures are inversely proportional to the volume.

Comparison of Values for the Coefficient of Enrichment K (Sorel).

The values of $\frac{1}{v} \log \frac{a}{a-x}$ for ethyl alcohol have already (see above) been calculated for two concentrations of the alcohol (0·81 per cent. and 4·81 per cent.), and an appreciable difference is observed between the two sets of results. In order to correlate the variation in the distillation coefficient with the coefficient of enrichment, a more extended series of solutions was studied. The concentrations of ethyl alcohol varied between 4·38 per cent. (by weight) and 0·24 per cent. The values of $\frac{1}{v} \log \frac{a}{a-x}$ for each concentration were determined, and the corresponding values of K calculated. The values obtained are recorded in Table IV.

The values of K obtained experimentally by Sorel varied from 7·15 at 5 per cent. concentration to 9·9 at 1 per cent. concentration. The calculated values of K agree approximately with those obtained directly (see Table IV), thus confirming the relation between the two coefficients we have already deduced.

It will be seen that the distillation coefficients of the alcohols increase in an approximately regular manner with an increase in the molecular weight. The occurrence of a branched chain in the compound results in an increased volatility, as shown by a comparison of the distillation results of the butyl alcohols. The trend of the figures is analogous to that in the case of the lower fatty acids. The fact that the solute of lower boiling point exerts a greater pressure in solution than one of higher boiling point is probably dependent on the fact that the attraction of the unlike molecules (alcohol for water) diminishes with rise of molecular weight of the alcohols, as shown by decreasing miscibility.

In connection with these comparisons it should be mentioned that there is often an evolution of heat and a volume change on mixing the alcohols with water. This is true, however, with large excess of water; but, for example, with sixty molecules of alcohol to forty of water there is an absorption of heat in the case of tertiary butyl, *n*-propyl, and *iso*-butyl alcohols. The contractions on mixing also diminish with rise of weight of alcohol (Young and Fortey).[1]

Table IV.

Concentration of Ethyl Alcohol.	$\frac{1}{v}\log\frac{a}{a-x}$ observed.	K calculated.
Per cent.		
4·8	·0173	7·96
2·6	·0179	8·23
1·75	·0187	8·60
1·14	·0191	8·79
0·74	·0190	8·74
0·38	·0214	9·27
0·24	·0207	9·50

It is seen from Table IV that the distillation coefficient is influenced by the concentration. This is not due to temperature effects, since it has been found that on calculating the value of K, it only diminishes slightly with increasing temperature, as in Table V.

[1] Trans. Chem. Soc., 1902, 81, 717.

TABLE V.

Concentration of Solution.	Temperature.	*K*
Per cent. 80·0	39·76	1·084
80·0	54·8	1·078
80·0	74·79	1·076
60·0	39·76	1·36
60·0	54·8	1·34
60·0	74·79	1·33

The values of *K* in Table V have been calculated from figures given by Vrevsky.[1] The value of *K*, and consequently all the distillation values, are dependent on the concentration of the solution—the greater the concentration the smaller the distillation coefficient. For aqueous solutions of the soluble alcohols of concentration less than that of the constant boiling point mixture the distillation figure increases with increasing dilution, reaching a maximum value in dilute solution. In very dilute solutions the values for the different alcohols are of the order of those recorded in Tables I and II. A comparison of these coefficients with vapour pressures at 100° of the various alcohols shows that there is no apparent agreement between the rates of distillation in aqueous solutions and the volatility of the alcohols.

Although these substances are associated in the pure state, it is improbable that the molecular complexes are not dissociated in very dilute solution. The lack of agreement between the rates of distillation of the aqueous alcohol mixtures and the volatility of the pure alcohol cannot be due to the presence of molecular association of the solute.

There is the possibility that soluble alcohols become associated in part with some of the solvent when dissolved in water; and, if it be assumed that only the free solute is volatile, the concentration in the vapour phase will be proportional to the concentration of the free substance in the liquid phase.

The evidence in favour of the associating theory is, however, very small in these cases. Against the hypothesis that there is any kind of combination or association of the alcohol with water, we have the fact that when the azeotropic mixture of *n*-propyl alcohol and water is cooled in a freezing mixture pure ice separates out. In addition, the formation of an azeotropic

[1] Zeit. phys. chem., 1912, 81, 1.

mixture of minimum boiling point indicates feeble attraction between the unlike molecules.

A more likely explanation may, however, be suggested to explain the results obtained. It is probable that the changes of concentration may bring variations in the "mass of water per c.c. in distillate." Any variation in this quantity will cause A to vary, even though Nernst's law still holds; we have

$$A = \frac{1}{\text{volume distilled}} \log_{10} \frac{\text{initial amount of alcohol}}{\text{amount of alcohol distilled}},$$

and k is related to A thus—

$$A \times \text{constant volume in flask} \times 2{\cdot}3026 = k \frac{\text{mass of water per c.c. in distillate}}{\text{density of water vapour in flask}}.$$

If variations exist, it might be more satisfactory—instead of calculating from the total distillate as shown in Table I—to calculate A from each separate fraction. This we can do, since the volume is kept constant. Table VI gives the new results then obtained.

Table VI.

Initial mass of Ethyl Alcohol in grams per 100 c.c.	Weight of distillate.	Mass of water per c.c.	$\frac{A}{\sigma}$
4·81	8·71	0·795	0·0218
	10·81	0·860	0·0208
	10·12	0·905	0·0206
	9·74	0·945	0·0202
	9·92	0·945	0·0202
	9·98	0·945	0·0184

The mass of water per c.c. has been calculated from our analyses and from density tables. The value of $\frac{A}{\sigma}$, it will be observed after correction, gives practically the same value as for dilute solutions, for which σ = 1 approx.

If we take the mean values, omitting first and last determinations, we get $\frac{A}{\sigma}$,

first set (0·81) . . . . 0·0208,
second set (4·81) . . . . 0·0204.

The variation in the weight of water per c.c. of distillate appears to account for the variation in A with concentration within the limits of experimental error; $\frac{A}{\sigma}$ gives the limiting value of A for very dilute solutions.

Preparation of n-Butyl-n-butyrate.

In the estimation of *n*-butyl alcohol with potassium dichromate and sulphuric acid, it was previously noted that some ester was formed when the oxidation was carried out under certain conditions. The conditions which facilitate the formation of this ester were studied as a separate problem.

n-Butyl alcohol (148 grams) was added to a solution of potassium dichromate (200 grams) in sulphuric acid (276 grams in 750 grams of water). Precautions were taken during the addition of the alcohol to prevent the temperature from rising above 30–40°, otherwise the reaction would tend to become vigorous, especially when the alcohol is added too quickly. When the addition was complete, the reaction-mixture was heated for 2–6 hours on a water bath. If the oxidation proceeded satisfactorily, a light-coloured oil was obtained, with a quantity of dark-green lower aqueous layer.

The oil consisted chiefly of *n*-butyl-*n*-butyrate, together with a small amount of unchanged alcohol and products boiling above 190°, and usually a trace of butylaldehyde. In the best experiments a 75 per cent. yield of *n*-butyl-*n*-butyrate was obtained on the original weight of alcohol taken. During some of the experiments, notably those in which the duration of heating was short, the ester layer was contaminated with a green substance. This substance contained chromium, and appeared to be slightly volatile in the vapour of *n*-butyl-*n*-butyrate, for, on distillation of the crude ester, the main fraction was coloured green. It was obtained in a crude state by removing the volatile portions from the residue remaining in the flask after distillation. It was a dark-green amorphous mass, readily soluble in acetone.

As a product of the reaction there was always present a small amount of a substance of higher boiling point than *n*-butyl-*n*-butyrate. The yield of the substance was found to be increased by allowing the oxidation to be completed at laboratory temperature.

The formation of the *n*-butyl-*n*-butyrate may be explained by assuming the intermediate formation of butyric acid which is esterfied by the alcohol. Butyric acid, in fact, has been detected from the aqueous layer, and is usually a product of the reaction.

The following gives a typical example, showing the yields obtained :—

From 150 grams of *n*-butyl alcohol by oxidation the product had the following composition :—

n-Butyl alcohol . .	17·5 grams.
n-Butyl-*n*-butyrate . .	109·4 „
High boiling-point fraction .	3·0 „
n-Butyric acid . . .	8·0 „

The amount of ester obtained is approximately 75 per cent. of the theoretical yield calculated on the alcohol taken.

The ester was identified by hydrolysis yielding *n*-butyric acid and *n*-butyl alcohol. The boiling point of the ester is 166·7°/761 mm.

The authors wish to state that they are much indebted to both Professor Sydney Young, F.R.S., and Dr. F. E. Hackett for many suggestions and useful criticism. They also take this opportunity of expressing their thanks to Captain Desborough for his interest in this work, and for securing permission for publication.

XXII.

THE "BROWNING" AND "STEM-BREAK" DISEASE OF CULTIVATED FLAX (*LINUM USITATISSIMUM*), CAUSED BY *POLYSPORA LINI* n. gen. et sp.

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[COMMUNICATED BY DR. GEORGE H. PETHYBRIDGE, B.SC.]

[PLATES VIII–X.]

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I.—INTRODUCTION.

DURING the recent European war a heavy demand for flax fibre from home-grown sources arose, consequent on the cutting off of foreign supplies. Since, owing to the high prices for fibre then prevailing, successful cultivation of flax was highly remunerative to the farmer, it is not surprising that a boom in flax cultivation set in, so that an immediate and large increase in the area under this crop in Ireland resulted.

This was accompanied in not a few instances by partial or total failure of the crop, which on inquiry and investigation often proved to be due to such causes as unsuitability of soil and unsatisfactory methods of cultivation and manuring, as well as to the use of inferior seed.

In a considerable number of cases, however, it appeared evident that specific diseases caused by parasitic organisms were responsible for serious trouble, and the insufficiency of our knowledge of flax diseases became acutely felt.

Stimulated by this lack of information, a programme for the scientific investigation of flax diseases was forthwith embarked upon by the Seeds and Plant Disease Division of the Irish Department of Agriculture.

A general account of the work undertaken and of the results so far obtained has recently appeared in the Department's Journal,[1] and a scientific

[1] Pethybridge, G. H., and H. A. Lafferty, "Investigations on Flax Diseases," Jour. Dept. Agric. and Tech. Inst. Ireland, xx, 3, 1920, p. 325. See also xxi, 2, 1921, p. 167.

paper dealing with one new specific disease, "Seedling Blight," has also been published.[1]

The present paper deals with another previously unrecognized disease of flax which has been proved to be caused by a fungus hitherto undescribed, and in which a general "browning" of the crop, accompanied by the fracture of many of the stems of the plants, are characteristic features. Up to the present this disease has not been described as occurring in any other country. Nevertheless, there is reason for believing that it must occur elsewhere; and it seems not improbable, from a preliminary note on a disease of flax in Holland, provisionally ascribed to a species of Gloeosporium, published in 1914, that the case in question was one of "browning."[2] The disease occurs in Ireland on flax grown from Dutch seed rather more frequently than on crops grown from seed from other countries. The fungus causing it has been found on seed derived from crops grown in England and Scotland and on seed believed to have been raised in Belgium. The disease has appeared in Ireland on crops from seed purporting to have been raised in England, Scotland, Holland, Russia, Canada, and Japan, and it is believed to be present in British East Africa.

II.—Symptoms of the Disease.

As stated above, the disease manifests itself in two principal forms, and for these the popular terms "browning" and "stem-break" are suggested as suitable.

1. *General features*—(*a*) "*Browning.*"[3]—To the casual observer "browning" first becomes evident about pulling time. The actual time depends to a large extent upon the earliness or lateness of the particular season, but in normal years it is usually towards the end of July or the beginning of August. At this time isolated areas in the crop, of various shapes and sizes, take on a distinct brown colour, so that they contrast somewhat strongly with the still green surrounding plants. Gradually these patches increase in extent until they coalesce, and the entire field becomes more or less uniformly brown. Occasionally, when primary infection is more general from the start, "browning" develops in a more or less uniform fashion over the whole crop, instead of appearing first in isolated areas.

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[1] Pethybridge, G. H., and H. A. Lafferty, "A Disease of Flax Seedlings caused by a Species of Colletotrichum and transmitted by infected seed," Sci. Proc. Roy. Dub. Soc., xv. (N. S.), 30, 1918, p. 359.

[2] Meded. v. d. Rijks Hoogere Land-, Tuin- en Boschbouwschool, Wageningen, vii, 1914, p. 53.

[3] "Browning" is sometimes, but erroneously, referred to as "firing." True "firing" is a very different disease, and is caused by *Melampsora lini*, one of the rust fungi.

The rate of development of "browning" is intimately connected with the weather conditions prevailing at the time, being more rapid in damp warm weather than under relatively dry atmospheric conditions. One diseased centre, approximately one square foot in area, kept under observation, was found to have increased in three days to an irregular area of about seventy-two square feet. Some farmers have long recognized the epidemic nature of the trouble, and they endeavour to pull the crop as soon as "browning" makes its appearance

When individual plants collected from a "browned" patch are carefully examined, it is seen that the fruits, sepals, leaves, and stems show brown diseased areas on their surfaces; and it is to the effect of these when seen in mass that the general browning of the crop is attributable.

On the still partially green leaves the diseased spots, which are generally rounded in outline, may occur either singly or in considerable numbers, as many as eight having been counted on a single leaf. They are dark brown in colour, and, as a rule, sharply marked off from the surrounding tissues, while they are slightly depressed below the level of the normal leaf-surface. As the spots do not increase in size very rapidly, the affected leaves remain only partially attacked, and are able to continue their functions to a considerable extent for some time after infection. In those cases, however, where a leaf becomes attacked in the region of its petiole, death of the whole leaf quickly ensues. In all cases, irrespective of the region of attack, an affected leaf dies prematurely, turns brown, and either falls off the plant or remains with its surface adhering to the stem.

On the main stem the diseased areas are often closely associated with the presence of a diseased leaf situated at a slightly higher level. They are first apparent as minute elongated spots, which are light fawn to brown in colour. Gradually the spots increase in size, especially in a longitudinal direction, and they may even coalesce, laterally as well as longitudinally, until practically the entire surface of the stem is involved (Plate VIII, fig. 2).

In dry weather the cortex often ruptures lengthways along a diseased area, and the stem, when bent at right angles at such a place, has a strong tendency to break; such a brittle condition is, of course, quite foreign to healthy flax.

The attack on the branches is similar to that on the main stem; but, owing to the smaller diameters of the former, the diseased areas more frequently encircle them completely.

Diseased sepals turn brown, and generally adhere firmly to the wall of the fruit.

Affected fruits are easily identified in the earlier stages of attack while

they are still green, but as they ripen they lose their green colour naturally, and become golden or light brown in colour. At this stage the recognition of the disease becomes almost impossible without the aid of the microscope. On the green fruits the diseased areas may arise at any point, but they are generally located at the apex or along one of the five raised ribs. They are, at first, light fawn in colour, and often surrounded by a darker zone due to the development of anthocyan. Gradually, as the disease advances, the darker zone becomes involved, and the colour of each area may then vary from fawn to brown. Fruits showing various stages of attack are illustrated in the two upper rows of fig. 3, Plate VIII. Whether infection originates at the apex or along a ridge, the diseased tissues lose moisture and contract, with the result that affected fruits show a strong tendency to gape open, especially in very dry weather.

As the fruits become ripe and dry, the progress of the disease is retarded; hence many of them show infection on one side only, or on a restricted area about the apex. But in cases of early infection the entire fruit may become diseased, and, if opened, the young seeds within are found to be shrivelled and dead. In cases of slight infection the seeds may appear normal to the naked eye; but, as will be shown later, the majority of them, though still retaining their vitality, are, nevertheless, heavily infected with the disease.

(*b*) *Stem-break.*—In a crop suffering from "browning" there are to be found individuals here and there which, instead of standing upright like the majority of their neighbours, have their stems bent over and lying on the ground. The recumbent position of these stems is due to the fact that at or in the region of the first node they are diseased, and have, therefore, become more or less completely broken across (Plate VIII, fig. 5).

When the fracture is practically a complete one, the plants turn yellow, die, and finally become brown. If, however, the stems are already fairly well developed before the attack becomes severe, and if, therefore, a considerable development of woody tissue has already occurred, only partial fracture occurs. The stems bend over, but since the conducting tissues are not entirely severed, the portions above the breaking-point continue to live and grow for a time. They develop negatively geotropic curvatures, as is shown in Plate IX, fig. 1, but ultimately they succumb prematurely. The connexion between "stem-break" and "browning" was not at first recognized; but, as will be explained later, it has now been proved that these two dissimilar phenomena are due to one and the same cause.

2. *Histological features.*—Microscopical preparations of the tissues from any of the affected parts of flax plants show the presence of hyaline, septate, and branched fungus hyphae in the diseased tissues. The cell contents are

brown and disorganized, while the chlorophyll granules are destroyed. Cross-sections of flax stems in the early stages of the disease show fungus hyphae permeating the parenchymatous tissues of the cortex and travelling in the cells between the fibre bundles. Fungus hyphae have never been observed penetrating the fibre bundles themselves or extending into the wood. A cross-section through a partially diseased stem is shown in Plate VIII, fig. 4.

In such cross-sections the individual fibres of the bundles running through a diseased portion of the stem usually have somewhat thinner walls and larger lumina than those of normal fibres in a healthy region of the stem. Owing to the shrinkage consequent on the death of the epidermal and cortical cells, the fibres are somewhat flattened tangentially.

Micro-chemical tests show that the fibre bundles in a diseased region undergo certain changes in composition. Thus, with Schulze's solution, the thickened parts of the fibre walls slowly become violet in colour, while the middle lamellae are stained yellow. The walls of normal fibres when treated with this reagent quickly become blue, while the middle lamellae remain undifferentiated. When cross-sections are treated with concentrated sulphuric acid, the thickened walls of the fibres in a diseased region swell up and become dissolved; but the middle lamellae remain insoluble, and present the appearance of a brown cellular skeleton. In a healthy region the middle lamellae also disappear. With a solution of iodine in potassium iodide the middle lamellae of the fibre bundles in a diseased region are coloured yellow, while the thicker portions of the fibre walls remain unstained. Phloroglucin stains the wood a bright red in all regions; but in a diseased region it also stains the middle lamellae of the fibre bundles red, whilst the walls of the individual fibres themselves are also to some extent reddened. This does not occur with normal fibre bundles; and the reactions suggest that lignification of the walls of the fibres has to some extent occurred. Correlated with this change is, doubtless, the fact already alluded to, that at diseased regions the stems become somewhat brittle.

Since, as will be seen later, the disease is one which is transmitted by means of the seed, special attention was paid to the manner in which the seeds become infected with the fungus. For this purpose, fruits at all stages of development were collected and studied microscopically by means of cross-sections. The progress of the mycelium was traced from the outside of the fruit through the tissues of its walls to the placenta, until it reached the seed itself by traversing the extremely short funicle. If the seeds are young, and the several layers of the seed-coat consequently not fully developed, the fungus penetrates these tissues, and reaches the young embryo, which becomes

permeated with mycelium, and is killed. Such dead seeds eventually become covered externally with conidia, and, as a rule, remain adherent to the inner walls of the fruit.

If the seeds are more nearly ripe before infection of the fruit occurs, the fungus, as before, reaches the two outer layers of the seed-coat, but does not penetrate the third or fibrous layer. Hence the embryo remains secure from attack, and its subsequent development proceeds normally. Although unable to gain entrance to the embryo, the fungus often continues to spread in the outer layers of the seed-coat, and produces conidiophores and conidia on the surface of the seed.

As the infected seeds become ripe they break away from the placenta, and the fungus produces conidiophores and conidia in great abundance on the resulting scar. Slightly affected seeds show the presence of conidia only at or in the region of the hilum.

3. *Details of the Fungus.*—When portions of affected plants, whether stems, leaves, sepals, or fruits, are kept for forty-eight hours or so in a moist atmosphere, minute beehive-shaped pustules (*acervuli*), scarcely visible to the naked eye, are produced on and around the margins of the discoloured diseased areas.

These acervuli, which occur, as a rule, directly over the stomata, are gelatinous in consistency and hyaline to milky in appearance. They are made up of large numbers of conidia, produced by groups of conidiophores, the swollen tips of which emerge only slightly through the stomata. One such conidiophore emerging on the surface of a diseased leaf and producing conidia is shown in Plate X, fig. 5.

Occasionally on diseased stems and branches, especially when the disease has advanced to a very considerable extent, cases are met with where masses of conidia are to be found in minute pockets beneath the epidermis, as well as on its surface. These submerged conidia are produced by conidiophores which at first produced conidia in the sub-stomatal respiratory cavity. Eventually, however, owing to the pressure from beneath, the epidermis bursts, and the conidia are forced out in bulk. Conidia have never been observed to be extruded through a stoma in the form of a tendril, as takes place commonly in the case of a pycnidium with an ostiole. This submerged production of conidia has never been observed on leaves, and, though sometimes seen on stems and branches, it is not the usual method. In the majority of cases conidia are produced outside of the host.

The acervuli have been examined carefully in all stages of development, and on all parts of the host plant for the presence of setae, but the latter have never been met with.

The conidia, which have bluntly pointed ends, are hyaline, single-celled, and of varying shape—oval, cylindrical, and straight forms with a peculiar basal twist are those most commonly met with: see fig. 1, Plate X. Stained preparations reveal the fact that the wall of each conidium is slightly thickened at its base, where it was attached to the conidiophore. Their contents are finely granular, and they sometimes possess one or more oil-drops. Though very uniform in breadth, which averages 4μ, they vary greatly in length, the extremes being 9μ and 20μ, with an average of 15μ.

They are produced by abstriction on the swollen ends of the conidiophores, and occasionally for a short distance along the sides of the latter. Each conidiophore may produce from one to seven conidia at a time; but three, four, and five are most often seen. When the conidia are ripe they become detached from the conidiophore, and new ones are then produced. Owing to the adherence of the conidia to one another, a little heap or mound of them is formed where the free ends of the conidiophores emerge.

In the case of the leaf, the conidiophores arise from a loose mass of hyphae situated towards the base of the respiratory cavity beneath a stoma. These hyphae resemble those that permeate the dead tissues of the leaf; but they are not sufficiently numerous or so densely packed as to permit of the aggregation of them formed in the respiratory cavity being regarded as a stroma. The conidiophores continue to grow in the form of an aggregation of rather thick hyaline parallel hyphae towards the stoma, through which their tips eventually emerge. As a rule they are simple, but occasionally they are seen to branch in an irregular manner. On emerging, their free ends, which never protrude very far, immediately become slightly swollen, and they begin to produce conidia. Simple unbranched forms were found to measure on an average 27μ long by $6{\cdot}5\mu$ broad, the latter measurement being made across the broadest part of the swollen apex.

On flax stems the formation of the conidiophores and conidia resembles in general that on the leaf. In some cases, however, especially when the cortex of the stem is in an advanced stage of disorganization, the parenchymatous tissues beneath the epidermis become ruptured, and the cavities thus formed become filled with a more compact mass of hyaline hyphae from which, here and there, conidiophores arise. These, if they have sufficient space, may produce sub-epidermal conidia as previously described, but more frequently they burst out through a stoma and produce conidia on the surface of the stem.

As already pointed out, this somewhat compacted mass of hyphae is by no means constantly associated with attacked stems, and even when present it is not sufficiently well developed to merit the description of a stroma.

The swollen ends of the conidiophores have been very carefully examined for the presence of sterigmata, but these have never been seen. Occasionally very minute local thickenings have been found in the walls at the ends of old empty conidiophores, which may, perhaps, represent points at which conidia were produced, but no general thickening of the wall of the conidiophore has been observed.

III.—Isolation of the Fungus and Behaviour in Pure Cultures.

Owing to the abundance of conidia produced by the fungus, there is no difficulty in obtaining it in pure culture. Such cultures, starting in each case from a single conidium, have been derived from the fungus present on diseased fruits, seeds, leaves, and stems, as well as on the affected tissues of plants exhibiting the "stem-break" phase of the disease. In every case detailed studies proved that the organism obtained was the same. It is easily cultivated and grows reasonably well on a variety of nutrient media.

Diluted conidia-suspensions in wort gelatine, or beef-extract gelatine, were plated out in Petri dishes in the usual way. When the gelatine had solidified, the dishes were examined with the low power of a microscope, and the positions of isolated conidia were marked. When germination had commenced, a single germinating conidium, together with a small piece of the medium surrounding it, was transferred, with aseptic precautions, to each of several tubes of slanted media; hence the growth in each tube was the product of a single conidium.

For purposes of comparison, the fungus isolated from different parts of the host and from flax plants growing in widely different localities in Ireland has been grown on the following media:—beef-extract gelatine, beef-extract agar, extract of Quaker-oat agar, ground Quaker-oat agar, cooked green flax stems and nutrient agar made from the watery extract of cooked green flax stems; but irrespective of its source of origin, the fungus behaved similarly on the various media used, and showed no morphological or cultural differentiation into strains or races.

The fungus develops its mycelium comparatively slowly and sparsely on all the media tried, but conidia are always produced in great abundance. On *beef-extract gelatine* and *agar* growth is poor, the mycelium being, for the most part, submerged. It is hyaline, septate, and branched, the individual cells being thin-walled and irregular in size and shape, and frequently much swollen. The surface of the medium becomes covered with a cream-coloured mass of conidia resembling a bacterial growth. The conidia are somewhat larger on the gelatine medium than they are on the host, their dimensions averaging $15\mu \times 5\mu$. On agar they averaged $14\mu \times 4{\cdot}6\mu$. Many of them

showed the production of new conidia from their ends. The gelatine is slowly liquefied, the process not being complete even after four weeks. Agar is not affected.

Cold water *extract of Quaker-oat agar* is a poor medium for the growth of the fungus. The amount of mycelium produced is relatively small, but dirty white masses of conidia are produced in good amount on the surface of the medium. The conidia averaged $13{\cdot}7\mu \times 4\mu$ in length and breadth respectively; and in shape they closely resembled those produced on the host plant.

Ground Quaker-oat agar was found to be the best medium for long-continued growth. On it the fungus grows slowly, but continues growing until the entire surface of the slant is covered, this being accomplished in about one month. The mycelium is again submerged, and conidia in cream-coloured, slimy masses are produced in abundance on the surface of the medium. After growing for several days, the submerged mycelium gradually becomes dark in colour, and as time goes on this darkening increases in intensity until a dense wrinkled mass of matted black mycelium is produced at or immediately below the surface. When examined microscopically, the dark mycelium is found to consist of much-swollen, more or less spherical thin-walled cells, with finely granular contents. Individually these cells are olive brown in colour, but when seen in mass the effect produced is almost black. The individual swollen cells of this dark mycelium eventually break away from one another, but their subsequent behaviour was not followed. It is believed, however, since they have never been seen in the tissues of the host plant, and are produced only on certain nutrient media, that they have no special significance in the bionomics of the fungus. Occasionally the olive tinge was taken up by the conidia or was diffused into the substance of the medium. As a rule, however, the conidia are hyaline, except where they are in intimate contact with the dark hyphae, and they averaged $14{\cdot}5\mu \times 4{\cdot}1\mu$ in length and breadth respectively.

The fungus grows well on *cooked green flax stems*, and produces acervuli on their surfaces. These acervuli are only just visible to the naked eye as very minute black dots resembling pycnidia. Microscopical examination shows that each conidial mass is in reality hyaline or milky in appearance, but, as it is seated on a dark-coloured base made up of the conidiophores whose swollen apices in this case are olive-coloured, it appears to have a smoky tinge. The conidia in the acervuli are similar to those found on the living host, and average $14{\cdot}3\mu \times 3{\cdot}8\mu$.

The mycelium in the tissues of the cooked flax stems is thick, hyaline, and much septate, the darkening only showing where the conidiophores burst through the epidermis.

Cooked green flax-extract agar is an unsuitable medium for the growth of the fungus; the submerged mycelium is sparse, with a complete absence of discoloration. Slimy, dirty white masses of conidia are produced on the surface of the medium, and, to a lesser degree, conidia are formed in the medium itself. They are very variable in shape and size, but average $15\mu \times 4{\cdot}3\mu$.

On all the media mentioned the conidia are produced in masses from the swollen tips and along the sides of the hyphae, which are little, if at all, differentiated from the ordinary mycelium, and which, therefore, scarcely deserve description as definite conidiophores. On the sides of the hyphae or on surface mycelium they are produced, one or more at a time, on the apices of short, blunt "pegs," which jut out from the cell wall, but which are very distinct from sterigmata; see fig. 6, Plate X. On the ends of the hyphae, which, as a rule, are slightly swollen, the conidia are produced by abstriction, and they may arise at any point; see fig. 3, Plate IX.

It sometimes happens that if, for some reason or other, a cell of the mycelium loses its protoplasm, the neighbouring cell behaves as a conidiophore, and conidia are produced in succession from it, and are pushed into the empty cell. Such a case is shown in fig. 8, Plate X.

The germination of the conidia, taken from the host as well as from pure cultures, has been followed in hanging drops of tap water, of the liquid extract of cooked flax, and also on film cultures of beef-extract gelatine, wort gelatine, and extract of oat agar.

In tap water, before germination, the conidia become much swollen, and in many cases two-celled, by the formation of a transverse septum. This causes a constriction in the middle of each conidium. From either or both ends of the conidia new conidia are produced, but no germ tubes are developed.

Where nutrients are used, however, the conidia swell rapidly, and in almost every case a transverse septum is produced, previous to the emission of a germ tube from one or both ends of the swollen conidium. As a rule these germ tubes soon become branched, and begin to produce new conidia at their ends after they have grown a short distance. Gradually, however, they increase in length by the development of new terminal cells, and these in turn bear conidia at their ends and along their sides until a fungus growth results, with a small amount of mycelium, but an abundance of conidia. The germination of the conidia, their subsequent growth, and the production of new conidia are illustrated in figs. 2, 3, and 4, Plate X. On wort-gelatine film cultures the early form of growth of the fungus is distinctly star-shaped when seen under the microscope, as illustrated in fig. 2, plate IX; but, as growth proceeds, lateral branches are formed on the radiating hyphae, and the star-shaped effect becomes obliterated.

IV.—Description and Position of the Fungus.

During the long period in which the growth and development of the fungus have been studied, both on various media in pure culture and on its natural host, the flax plant, no method of reproduction other than by conidia has been met with. It is clear, therefore, that for the present, at any rate, it must be placed amongst the Fungi Imperfecti.

If emphasis be laid on its mode of development on the host, the formation of conidia in definite acervuli would suggest its inclusion amongst the Melanconiales. On the other hand, judging from its mode of growth as a saprophyte on various media, it might well be placed with the Hyphomycetes.

At the outset the fungus was provisionally ascribed to the genus Gloeosporium, but detailed study shows that it cannot remain there. The figure given by Lindau[1] of the conidiophores of *Microstroma Juglandis* Niessl emerging through a stoma recalls at once the behaviour of the flax fungus. The genus Microstroma has been placed amongst the Exobasidiaceae, but Maire's investigations[2] show that it should rather be classed amongst the Fungi Imperfecti. In any case, however, in this genus the conidiophores arise from a definite submerged stroma, and no such stroma is developed by the flax fungus. As a matter of fact, the characters of the latter do not admit of its being placed in any genus hitherto described; hence it becomes necessary to make it the type of a new one. Since one of its leading features is the production of large quantities of conidia, with relatively little development of mycelium, the name Polyspora is suggested for the genus which will find a place in the Melanconiales. It is characterized as follows:—

Polyspora nov. gen.

Mycelium, hyalinum, septatum, intra hospitem ramosum: basidia ex hyphis laxe in cavo substomatali conglomeratis surgentia ad summum subtumida et per stomata paullum protuberantia simplicia vel subramosa ad summum plura conidia quodque gerentia: acervuli numerosi minuti gelatinosi hyalini vel lactei in hospitis epidermide super stomata raro subter siti: conidia hyalina continua obovata vel cylindracea terminis rotundatis complura simul ad summos vel in lateribus basidiorum gesta.

P. lini. nov. spec. E genere supra descripto; conidiis 9–20μ (medium 15μ) longis 4μ latis nonnumquam cum una vel duabus guttulis.

Hab. in foliis, stirpibus, fructibus seminibusque vivis *Lini usitatissimi* in Hibernia.

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[1] Lindau, G., Rabenh. Krypt. Flora. I, 8, p. 19.

[2] Maire, R., La structure et la position systematique des *Microstroma* et *Helostroma*. Nancy. 1913.

V.—PROOF OF PATHOGENICITY OF THE FUNGUS.

Experiments which proved that Polyspora is pathogenic to flax, and was the cause of "browning" and "stem-break," were carried out under strictly controlled conditions in the greenhouse. Other experiments were carried out in the field, where, of course, less control of the conditions was possible. These infection experiments will now be dealt with.

Two small lots of flax seed, previously proved by microscopical examination to be free from fungus infection, were sown in pots of soil previously heated in an autoclave at 140° C. for two hours on each of three successive days. A perfectly healthy and luxuriant crop of seedlings arose, and the plants were allowed to grow until the petals of the flowers had fallen and the fruits were beginning to form. The plants in one pot, which served as a control, were then sprayed with sterile water and at once covered with a large glass bell-jar. Those in the second pot were sprayed with a suspension in sterile water of conidia from a thirty-day-old pure culture of the fungus, and were likewise covered with a large bell-jar.

The experiment was started in August, and the plants were left in an unheated greenhouse. They were carefully examined daily; but the bell-jars were not removed for this purpose. The first indications that infection had taken place were noticed on the twentieth day after spraying. Circular brown spots appeared on the leaves, and elongated brown areas on the stems and branches, of the plants which were sprayed with the suspension of conidia, thus reproducing the typical symptoms of "browning" as it occurs in the field. After a further lapse of a few days portions of affected leaves, stems, and branches were removed and examined microscopically, when typical acervuli, made up of the conidia and conidiophores of the fungus, were found on the diseased areas in all cases.

The conidia present in these acervuli were plated out, and the fungus obtained was proved by comparative tests in pure cultures to be identical with that from which the conidia used for inoculation purposes were obtained. At no time throughout the experiment did the control plants show any signs of disease whatever.

Two adjacent plots, containing only healthy flax plants, were selected among those on the land attached to the field laboratory. Each plot was four square yards in area, and when pulling time was near at hand the plants in one plot were sprayed with sterile water, while those in the second were sprayed with a suspension in sterile water of conidia from a sixteen-day-old pure culture of the fungus.

After a lapse of sixteen days the plants in the plot sprayed with the conidial suspension had become distinctly brown, and resembled in every detail those naturally affected with the disease. Those in the control plot assumed the normal golden colour characteristic of healthy ripe flax, and showed not the slightest trace of "browning."

The "stem-break" phase of the disease was also artificially reproduced in the following manner:—Two pots of soil were sterilized as before, and flax seeds proved to be fungus-free were sown in each. After sowing, the plots were covered with bell-jars and kept in the greenhouse. When the seedlings were about one and a half inches high all the cotyledons of the plants in one pot were wetted with sterile water, while the cotyledons of those in the second pot were smeared with conidia from a twelve-day-old pure culture of the fungus. The bell-jars were then replaced. During subsequent waterings of the soil care was taken not to wet the cotyledons; consequently the conidia remained undisturbed on them.

The smeared cotyledons showed the first signs of infection seventeen days after the conidia had been applied to them. They gradually turned brown, and, owing to the general infection which took place over their whole surfaces, isolated spots did not develop. The progress of the fungus along the cotyledons was followed until the latter reached the main stems of the plants at the nodes. Here it continued to spread, with the result that the tissues of the stem became diseased and brown; but its further progress was not rapid, and the injury was more or less localized.

Twenty-four days after smearing all the cotyledons were dead, brown, and shrivelled, and one plant had toppled over, the stem being nearly broken through a little below the first node. In this case the disease extended down along the stem for approximately half an inch; but the greatest damage to the tissues occurred where the partial fracture took place.

The experiment was continued for forty-six days, by which time five other plants had fallen over, the partial fracture of the stem being at the first node in each case; see fig. 1, Plate IX. The remaining plants were then carefully examined, and in every case their stems at the point of insertion of the cotyledons were found to be more or less diseased. Owing to the tranquil conditions prevailing underneath the bell-jar, they continued to remain erect, but had they been subjected to the disturbing effects of wind and rain, such as would be the case under open field conditions, many more of them would, in all probability, have fallen over.

The dead cotyledons and the diseased areas on the stems of those plants that had fallen over were examined microscopically, and typical acervuli of the fungus were found in abundance on them. Finally, it was proved by

raising pure cultures from single conidia of the fungus present that the latter was identical with the one used for inoculation purposes.

The plants in the control pot remained healthy throughout the experiment. In many cases their cotyledons lost their green colour and turned yellow, but no fungus appeared on them.

VI.—Disease Transmission.

During the inspection of large-scale field plots of flax derived from seed having different countries of origin, it was early recognized that the plants from certain kinds of seed, notably that imported from Holland, were often heavily attacked by "browning," while crops from seed from other countries, though grown under similar conditions, often actually side by side, were comparatively or quite free from it. Even before it was discovered that the seed itself is liable to attack, this observation strongly suggested that transmission of the disease probably took place in some way by means of the seed.

In several instances samples of the seed from which a diseased crop arose in the field were obtained, and in every case it was definitely proved by microscopical examination and cultural trial that such seed was infected with the fungus.

The method of seed examination for the presence of the fungus was as follows:—A number of drops of water were placed on a microscope slide, and a single seed from the sample under examination was placed in each drop and manipulated until it became thoroughly wetted. The drops were then examined microscopically with a low power. In the first few trials nothing abnormal was noticed. Eventually, however, conidia identical with those of *P. lini* were seen in abundance in the water surrounding one of the seeds; and, as the examination proceeded, numerous examples were found where a similar state of affairs occurred.

In the majority of cases where conidia were seen, the latter were present in masses around the hilum of the seed, and they floated away singly or in groups into the surrounding water. They were, however, by no means confined to this region, often being present over the entire surface of heavily infected seeds.

Several of these seeds on which conidia were present were more closely examined with a view to ascertaining whether the conidia were merely adhering mechanically to their surfaces or were associated with internal mycelium in the seed-coat. Transverse sections of such seeds when examined microscopically showed that the outer layers of cells of the seed-coat were permeated with hyaline, branched and septate hyphae; and the conidia were,

for the most part, formed on conidiophores which sprang from these hyphae and had burst through the outer wall of the epidermal cells. The conidiophores resembled those of *P. lini* as found on browned flax, but they were not grouped together as they occur when protruding through a stoma. They were more or less isolated, and emerged singly and in an irregular manner all over the surface of the seed, so that definite acervuli were not produced. At the hilum the conidiophores were produced in greater quantity than elsewhere. Two simple conidiophores producing conidia on the surface of a seed are shown in fig. 7, Plate X.

As has previously been stated, the fungus hyphae in the seed-coat can clearly be traced in the epidermal and underlying parenchymatous tissues as far as the outer edge of the fibrous cells, but they have never been seen to penetrate the latter.

Occasionally masses of conidia have been found completely filling individual cells of the dead parenchymatous tissue beneath the epidermis, and in some cases they are formed in the epidermal cells themselves. Generally speaking, however, they are produced on the exterior of the seed-coat.

Owing to the rupture of the cuticle and walls of the epidermal cells by the conidiophores of the fungus, affected seeds absorb water more rapidly than healthy ones do; consequently such seeds become mucilaginous more quickly, and this fact is an aid to their detection.

Trials were made to ascertain whether the conidia present on the seed-coat were alive, and, if so, whether they had any connexion with the outbreak of "browning" on the plants in the field. They were found to be alive, and by the ordinary poured plate method pure cultures (starting in every case from a single conidium from the surface of an affected seed) were raised. Further, by comparative cultural tests the fungus so obtained was proved to be identical with that isolated by means of the conidia taken from browned stems, leaves, and fruits.

As a result of microscopical examination, fifty-two seeds bearing conidia were picked out from a sample which had produced a browned crop the previous year. These seeds were sown approximately one inch deep in a pot of sterilized soil, and after sowing the pot was covered with a bell-jar and kept in an unheated greenhouse. Since the seeds were sown in October, germination was slow, and the plants, which were examined daily, made poor growth.

The first sign of disease was noticed on the thirtieth day after sowing. The cotyledons of several of the seedlings showed little brown rounded areas, which gradually increased in size and became dark in colour. The experiment

was concluded on the thirty-third day after planting, and out of a total of forty-six plants fourteen showed diseased cotyledons. As the seedlings had not been watered, and the bell-jar was not removed before the appearance of the disease on the cotyledons, their infection must have resulted from the fungus present on the seeds sown.

Diseased cotyledons from the infected seedlings were examined microscopically, and it was found that the brown tissues were filled with hyaline, septate, and branched hyphae, while groups of conidiophores were bursting out through the stomata and producing conidia in typical acervuli of *P. lini* on the surface. Isolations of the fungus, starting in each case from a single conidium from one of these acervuli, were made, and in every case it proved to be identical with the species found on the leaves, stems, fruits, and seeds of browned plants. This experiment shows that the disease is capable of transmission by means of infected seed.

As is well known, flax seeds when sown and lightly covered with soil germinate, and in a great many cases their seed-coats are carried above soil-level, attached more or less loosely to the cotyledons. Where infected seeds are sown it is obvious that the infection of the cotyledons may take place from the fungus present on the seed-coats borne aloft in the manner described. In the experiment described above a record was not kept of the number of seedlings which carried up their seed-coats, but, as the seeds were planted approximately one inch deep, the number must have been small.

In the spring of 1919 flax seeds from a sample which had produced a browned crop in 1918, and some of which were proved by microscopical examination to be infected, were sown out of doors in a plot attached to the field laboratory.

When the plants had brairded, many of the cotyledons of the seedlings showed the presence of one or more brown circular spots, which on incubation in a moist atmosphere produced acervuli typical of the "browning" fungus. From conidia present in the acervuli, *P. lini* was isolated and grown in pure cultures. Such diseased areas on the cotyledons, some of which are illustrated in fig. 1, Plate VIII, were thus found to be the incipient stage of "browning" as it occurs in the field.

Cotyledons attacked by *P. lini* resemble very closely those attacked with "seedling blight," and in some cases the two diseases at this stage can only be differentiated with the aid of a microscope. To the naked eye the injury due to the "seedling blight" fungus (*Colletotrichum linicolum*) is lighter in colour than that due to *P. lini*, and its progress is also more rapid. In the former case an infected leaf soon becomes entirely destroyed; and this is often followed by death of the seedling as a whole, owing to the formation of

stem lesions in the region of the soil-level which cause the plant to "damp off." In cases of attack by *P. lini* the affected spots on the cotyledons are darker in colour, and do not increase in area rapidly, so that the cotyledons remain alive for a considerable time after infection has taken place. True, as mentioned in an earlier part of this paper, lesions due to *P. lini* have been found on the stems of affected plants in the region of the first node, as a result of which the latter fall over; but this condition of things generally occurs at a later stage, when the flax is at least six inches high, and it in no way resembles "damping off," as found in "seedling blight."

When there is any doubt as to which organism is at work the matter can easily be settled by microscopical examination of the acervuli present on the diseased areas. If *P. lini* is responsible, these acervuli will agree with those herein described; but if *C. linicolum* is the active parasite, the acervuli will be found to be made up of conidia borne singly in succession on conidiophores, while from the bases of the acervuli long, black, tapering setae arise.

As the seedlings affected with *P. lini* grew in size, some of the new leaves produced became infected through various agencies, from conidia present on the diseased cotyledons. From these leaves, in turn, adjoining plants became infected, with the result that when the crop was half grown the disease was general, though not very obvious. Some plants exhibited the "stem-break" form of injury, and were either dead or dying, while the leaves of others were spotted, and in a few cases minute elongated brown marks were making their appearance on the stems.

This state of affairs persisted until after the plants had flowered and the fruits were beginning to be formed. Then the fungus became more virulent, possibly owing to the decreased vitality of the plants or to some change in the environmental conditions, and "browning" of the leaves, stems, branches, and fruits became most pronounced. Thus it is seen that the fungus which causes "browning" is present, though not to a large extent, on some of the flax plants, at least from a very early stage in their development.

VII.—Control of the Disease.

The losses due to "browning" and "stem-break" are, in many cases, very serious, although naturally it is a difficult matter to estimate them quantitatively with accuracy.

"Browned" stems tend to break in the regions of the diseased areas during scutching. Thus the fibre is shortened, and much of it escapes with the tow. Further, plants affected with "stem-break" may be dead and useless at pulling time, and, in any case, are most likely to be left behind when the crop is pulled.

The yield of seed from a "browned" crop is a reduced one, and, of course, its quality is inferior. In Ireland, generally speaking, no attempt is made to save flax seed for sowing, and such loss may, perhaps, be regarded as of no serious consequence. Nevertheless, the work of the Irish Department's Plant Breeding Division in recent years has clearly shown that high-class fibre-flax seed can be produced at home; and the experience of the late war shows the great risks involved in depending on foreign sources alone for the supply of flax seed. Hence the desirability of endeavouring to find some means of controlling the disease.

Persistence of the Fungus.—Polyspora lini, as already stated, has not been found to produce any reproductive bodies other than the thin-walled conidia already described. It has been found, nevertheless, that this fungus can remain alive in a dormant condition in the host tissues for considerable periods, and under seemingly adverse conditions. Thus, flax stems affected with "browning" and containing the fungus were pulled in July, 1920, and allowed to become air-dry in the laboratory. After being subject to these conditions for six months they were exposed to a moist, warm atmosphere in a covered glass dish. In the course of a day or so the fungus recovered its activities. Large numbers of new acervuli were produced on the surfaces of the stems; and the newly formed conidia were found to germinate normally when transferred to films of beef-extract gelatine.

Affected stems pulled a year earlier than those just mentioned, and kept under similar conditions for eighteen months, showed a very feeble development of acervuli when placed in a moist, warm atmosphere; and only a scanty development of conidia took place. Nevertheless, a few of the latter were found to be viable.

In the ordinary course of events, affected stems after pulling go into the retting pond; but what happens to the fungus under these circumstances has not yet been fully ascertained. Stems affected with "browning," pulled and retted in 1919, were air-dried immediately afterwards, and were kept in the laboratory in this condition for eighteen months. When placed in a moist, warm atmosphere at the end of this period, further growth of the fungus and development of new conidia could not be detected with certainty.

No experiments have as yet been carried out with affected stems, either retted or non-retted, exposed to ordinary outdoor weather conditions over the winter. From what has been said above, however, it would appear possible for the fungus to remain alive in affected flax stems over the winter, and for such stems to form starting-points for the infection of the crop in the following season. That the latter is actually the case, however, seems highly improbable.

In Ireland flax is always grown in rotation with other crops, so that on a

given field a second crop of flax normally follows a previous one only after an interval of six or seven years. It seems scarcely likely that affected stalks, left lying in the field after the first crop, could possibly be a source of infection in such circumstances. It is more probable that they would have disappeared entirely and the fungus with them. There is no evidence at present, at any rate, that the fungus can live as a saprophyte in the soil; nor is there any evidence that infection of the crop comes from the soil. Again, after retting, flax is spread on grass fields to dry, but such grass land is not in practice laid down to a crop of flax in the following season, and often not for some years. Even if a few affected stray stalks were left on such land, and assuming that the fungus was not materially injured during the retting process, it seems improbable that infection would occur from this source.

The "shives" (débris consisting of woody cylinder and cortex) which accumulate at scutching mills, where the fibre from the retted flax is mechanically separated from the rest of the stem, are sometimes used for bedding farm stock. It is conceivable that should the fungus survive the retting process it might ultimately reach the land again in manure derived from such material. It is believed, however, that even if it exists at all, this possible source of infection is of no practical significance; and, as has been already stated, there is no evidence at present that the disease is contracted from the soil.

Ensuring Healthy Seed.—On the other hand, it has conclusively been proved that "browning" and "stem-break" can be transmitted by sowing infected seed;[1] and it is believed that this is the most important, if not the only, means by which outbreaks of the disease arise. Control measures, therefore, centre around the question of the seed; and the most obvious precaution would be to avoid saving seed for sowing from a crop suffering from "browning."

It might be considered possible to save healthy seed from a diseased crop by pulling the latter before the fruits and seeds had become infected. An attempt was, in fact, made to do this, but, owing to the early date at which pulling was necessary, the quantity of seed saved was extremely small; and it was found to be altogether too immature to be of any use for sowing purposes.

Again, it might be thought possible to check "browning" and prevent infection of the fruits by spraying the affected crop with an appropriate fungicide. It might, indeed, be feasible to spray the marginal portions of a field of flax at the time when "browning" was beginning to become evident,

[1] Viability tests of the conidia present on infected seeds showed that they retained their vitality on the dry seeds for two years and six months after harvesting. In three years, however, the conidia were all dead. The germination of the seed in this period had, of course, greatly diminished.

in so far as they could be reached from the headlands; and such portions might possibly be sufficiently large to provide the requisite quantity of seed in a given case. But until it can be done from the air by a hovering aeroplane, or by a dirigible airship, or other such means, spraying a flax crop at such a time will not be a practicable proposition, since with present-day machinery the injury which would follow the trampling down of the crop would be irreparable. In addition to this, there is to be considered the effect which the adhering fungicide might have on the subsequent process of retting. Whether spraying at a much earlier stage would be feasible without injury, and, if so, whether it would be effective in preventing "browning," is a problem which has yet to be explored.

Mechanical Avoidance of Infection from Seed-coats.—Since primary infection occurs in the seedling stage, and is due to the transfer of the parasite from the infected seed-coats to the cotyledons, on which the former are borne above the ground, it might be thought possible to intercept such primary infection by preventing the carrying aloft of the seed-coats; that is, by deep sowing of the seed.

Healthy seed was sown in plots at depths varying from half an inch to three inches; but it was found that sowing at a greater depth than one inch resulted in the production of such a thin braird of weak seedlings that a reasonable crop was quite out of the question. Moreover, it was also found that sowing infected seed at a depth of one inch did not suffice in many cases to prevent the seed-coats being carried up on the cotyledons, and infection of the seedlings was found to occur under such conditions. Hence, control of the disease by deep sowing of the seed is out of the question from a practical point of view.

Seed Disinfection.—Considerable attention has been devoted to the question of disinfecting affected seed both by means of fungicides and by heat; and a summary of what has been done along these lines will now be given. At the outset it may be remarked that flax presents special difficulties in regard to treatment with most fungicides in solution or suspension in water, owing to the mucilaginous nature of the outermost layer of the seed-coat, and the tendency of the treated seeds to adhere together in a sticky mass when wetted, thus rendering sowing extremely difficult or quite impossible. Experiments are in progress with a view to finding a way out of this difficulty, but they have not yet been carried sufficiently far to warrant discussion here.

Preliminary trials were made with aqueous solutions of copper sulphate and mercuric chloride, as well as with Burgundy mixtures (copper sulphate and sodium carbonate solutions) of varying strengths. Formaldehyde both in aqueous solution and in gaseous form was also tried. Sufficient seed to sow

an area of about twenty-five square yards was treated in each case, and the plots were situated close to the field laboratory at Boghill.

Copper Sulphate.—Affected seeds were lightly sprayed with an atomiser with 5 per cent. and 10 per cent. solutions of copper sulphate respectively. After spraying the seeds were spread out and dried for twenty-four hours at 40°C. The treatment had no adverse effect on the germination of the seed when tested in the usual way. The plants arising from the treated seeds when sown in the field, however, were not free from the disease.

Mercuric Chloride.—Similar trials were made with 0·1 per cent., 0·5 per cent., and 1 per cent. aqueous solutions of mercuric chloride, and the percentage of germination of the treated seed was found not to be appreciably lowered. Seedlings arising from seed treated with the 0·1 per cent. solution were, however, seriously diseased. The stronger solutions were more efficacious in checking the disease, but neither of them suppressed it entirely.

Burgundy Mixtures.—Affected seeds were sprayed with Burgundy mixtures of different strengths made by neutralizing 2 per cent., 10 per cent., and 15 per cent. aqueous solutions of copper sulphate with the requisite quantities of sodium carbonate solutions. The seeds were then dried, and the adhering blue precipitate remained as a coating on their surfaces. Germination tests showed that the vitality of the seed was in no way injured by the treatment. It was found, however, that the plants derived from such treated seed were not less affected with "browning" and "stem-break" than were those derived from untreated seed sown in an adjoining control plot.

Formaldehyde Solution: Steeping.—Affected seeds were steeped (with occasional shakings to ensure thorough wetting) for periods of five and ten minutes in weak aqueous solutions of formaldehyde having strengths of 0·09 per cent. and 0·18 per cent. respectively. After steeping, the seeds were separated from one another, placed on absorbent paper, and then dried for forty-eight hours at 35°C. Tests were made before and after treatment both of the germination of the seeds and of the viability of the conidia of the fungus. The results are summarized in the following table :—

Strength of Solution.	Time of Steeping.	Germination of	
		Seed.	Conidia.
Untreated.	—	94 per cent.	Abundant.
0·09 per cent.	5 minutes.	94 ,,	,,
0·09 ,,	10 ,,	96 ,,	Nil.
0·18 ,,	5 ,,	80 ,,	,,
0·18 ,,	10 ,,	46 ,,	,,

Steeping in the stronger solution satisfactorily disinfected the seed, but retarded and seriously reduced its percentage of germination. Steeping for ten minutes in the weaker solution killed the fungus, and did not reduce the germination of the seed, while steeping for five minutes only in this solution did not kill the fungus.

A repetition of the experiments gave similar results, with the exception that steeping for ten minutes in the 0·09 per cent. solution did not kill all the conidia; a few were found still viable after treatment.

Owing to the sticking together of the steeped seeds, however, it was found difficult to treat a quantity sufficient for sowing purposes. Hence no plots were laid down with seed steeped in formaldehyde solution.

Formaldehyde Solution: Spraying.—In order to avoid, if possible, the disadvantages of steeping, attempts were made to disinfect flax seeds by spraying. Lots of half a pound each of affected seed, after having been spread out in thin layers, were sprayed by means of an atomiser with 20 c.c. of diluted formaldehyde solutions of varying concentrations. This amount of liquid was not sufficient to cause the seed to become mucilaginous. After atomising, the seed was dried for twenty-four hours at 40°C. It was then tested for germination, and the viability of the conidia present on the seed was also tested. The results are summarized in the following table:—

Strength of Formaldehyde Solution.	Germination of	
	Seed.	Conidia.
Untreated.	94 per cent.	Abundant.
0·09 per cent.	92 ,,	,,
0·37 ,,	94 ,,	Sparse.
0·48 ,,	85 ,,	Very sparse.
0·59 ,,	73 ,,	Nil.
0·74 ,,	63 ,,	,,
1·49 ,,	51 ,,	,,
3·74 ,,	22 ,,	,,
37·40 ,,	2 ,,	,,

It will be seen that a concentration of 0·59 per cent. of formaldehyde was required in order to kill all the conidia, but the germination of the seed so treated was considerably reduced. Higher concentrations had a more pronouncedly deleterious effect on the germination of the seed, while lower ones did not entirely kill the conidia.

Seed treated with 0·37 per cent., 0·48 per cent., and 0·59 per cent. solutions respectively was sown in experimental plots, and untreated seed was sown in a control plot alongside of them. The disease became evident in the control plot and in the 0·37 per cent. plot as soon as the crop had brairded, and these plots showed "stem-break" and "browning" well developed at the time of pulling. The disease appeared much later in the plot sown with seed treated with the 0·48 per cent. solution, and at pulling time "browning" and "stem-break" were less evident in this plot than in the two just referred to.

The plants derived from seed treated with 0·59 per cent. solution showed no signs of the disease, and they remained quite free from it through the season.

In the three cases where treated seed was sown, the crop was considerably thinner than that derived from untreated seed, and thinner than might have been expected, judging from the results of the germination tests of the treated seed. It is clear that by spraying affected seed with a limited quantity of a 0·59 per cent. solution of formaldehyde the disease can be suppressed. But the quantity of seed sown per unit area would have to be increased considerably to ensure a crop of sufficient thickness, if this mode of control were adopted; and this might not be a profitable undertaking.

Formaldehyde Gas.—Affected seeds were exposed to formaldehyde gas when driven off by the action of potassium permanganate on a concentrated solution, as well as when allowed to evaporate naturally from the solution into a confined space of air. The results so far obtained, however, have not been satisfactory, for, although the conidia are killed, the vitality of the seed is much too seriously affected. Seed treated by the latter method was sown, and the resulting plants arose and remained free from the disease, but they were very few in number. It is hoped to carry out further trials with this gas, paying special attention to time of exposure of the seed and temperature of the gas.

Heat.—A good deal of experimental work was done in connexion with the effect of heat on flax seed. Thus, infected seeds were subjected to a temperature of 50°C. for periods varying from six to one hundred and ninety-two hours. The effect on the fungus was *nil*, the conidia germinating just as vigorously after heating as before, while the general effect on the seed was to improve its percentage of germination.

The conidia on affected seeds were also found to be unharmed by exposure to a temperature of 70°C. for periods of from three to seventy-two hours. Tests of the seed made just after treatment showed a considerable depression in the percentage of germination, but after a period of rest, at room

temperature, this percentage regained its normal amount. Similar results followed heating to 75° C. and 80° C. for periods up to 120 and 168 hours respectively.

Affected seeds were ultimately heated at 96·5°C. for periods varying from three to thirty hours. The conidia survived a twenty-four-hour period of treatment at this temperature in a viable condition, but not one of thirty hours. Seed heated to this temperature for so long a period, however, was found to be permanently injured. It is true that the percentage of germination improved somewhat after a period of rest at room temperature, but it never subsequently reached that of the unheated seed, the highest being 54 per cent., while that of the unheated seed was 94 per cent.

Seed treated in this manner was sown in a plot, but, as was to be expected, the resulting stand of plants was very thin. Moreover, they showed a lack of vigour from the start, and they remained much stunted and dwarfed promising a very poor yield of fibre. Nevertheless, the plants remained entirely free from "browning" and "stem-break" throughout the season.

From what has been said it may be inferred that the solution of the problem of disinfecting infected flax seed without injuring the seed itself is not an easy one.[1] Still, it is not to be regarded as hopeless, but rather as one requiring more intensive investigation; and further experimental work on the matter is already in progress.

No special study has yet been made regarding the question of the possible existence of strains or varieties of flax resistant or immune to the disease. But it has been observed, contrary to what was thought in some quarters, that both blue- and white-flowered varieties are liable to attack.

VIII.—Summary.

The present paper is concerned with a serious disease of flax which occurs in the field in two forms, viz.—(1) "browning," a turning brown of the plants, which occurs rapidly, especially under moist weather conditions, at or before pulling time; and (2) "stem-break," the fracture or partial fracture of the stems of a certain proportion of affected plants, usually in the region of the first node, and thus at or near soil-level.

One and the same fungus was found constantly associated with the disease in both of its forms.

[1] In the trials made so far, death of the conidia present has been taken as the criterion of disinfection of the seed. But it must be remembered that mycelium is also present in the tissues of the seed-coat; and this may possibly remain alive and capable of developing new conidia when those already present are killed.

This fungus was isolated, studied in pure culture, and was proved by means of controlled inoculation experiments to be the cause of both "browning" and "stem-break."

Not having previously been recorded, the fungus is described under the name *Polyspora lini* n. gen. et. sp.

Diseased plants produce infected seed, and it was proved that transmission of the disease occurs through the sowing of such seed. It is probable that this is the chief, if not the only, means by which the disease is perpetuated.

The fungus has been found on flax seed definitely known to have been produced in England and Scotland, as well as on seed purporting to have come from a crop grown in Belgium. It has also been found on flax grown in Ireland from seed believed to have been derived from crops grown in England, Scotland, Holland, Russia, Canada, and Japan, and the disease has been reported as being present on flax in British East Africa. It would appear, therefore, that the disease must be present practically wherever flax is cultivated. It is possible, however, that, owing to different climatic conditions, it may not be so serious in certain of these countries as it is in Ireland.

Seed for sowing purposes should not be saved from a crop suffering from this disease. Seed disinfection trials on a small scale have shown that atomising with a dilute aqueous solution of formaldehyde is one of the most promising means of control when healthy seed is not available for sowing.

Both white-flowered and blue-flowered varieties of flax have been found susceptible to the disease.

EXPLANATION OF PLATES.

PLATE VIII.

FIG.

1. Naturally affected flax seedlings, seen from above, showing dark diseased areas on the cotyledons, attacked by *Polyspora lini*, which represent the earliest stage of "browning." (Slightly enlarged.)

2. Portions of stems of mature flax plants, showing various stages of the "browning" disease. That on the extreme left shows spotting of the leaves only. Death of the leaves and infection of the stems is evident on the remaining four. (× ⅓.)

3. Bottom row: healthy flax fruits. The upper two rows show affected fruits in various stages of attack. (Natural size.)

4. Transverse section through a mature flax stem affected with "browning." The dark diseased cortical and epidermal tissues extend nearly, but not quite, around the stem. (× 30.)

5. Five naturally affected young flax plants, showing stages in the development of "stem-break." The two on the extreme left show cotyledonary infection only; the two on the extreme right have their cotyledons destroyed, and infection of the stems at the node has occurred, with incipient break. The central one shows an intermediate stage. (Slightly reduced.)

PLATE IX.

1. "Stem-break" produced by placing conidia of *P. lini* from a pure culture on the cotyledons of seedlings. In all cases the stems became attacked, and fracture of the stem, with subsequent upward bending, is well marked in four cases. (Slightly reduced.)

2. Stellate form of growth of *P. lini* on wort gelatine from a single conidium; culture five days old. The masses of conidia are seen along the radiating hyphae, which are, however, invisible in the photograph. (× 30.)

3. Conidia formation in *P. lini*, from a five-day old pure culture on a wort gelatine film. (× 270.)

Plate X.

All figures × 510 diameters.

FIG.

1. Conidia of *Polyspora lini* from a naturally affected flax leaf.
2. Conidia germinating on beef-extract gelatine; twenty-four hours old culture.
3. Same as 2; forty-eight hours old culture, new conidia being produced.
4. Same as 2 and 3; seventy-two hours old culture.
5. Vertical section through portion of an affected flax leaf, showing one conidiophore of *P. lini* protruding through a stoma, and producing conidia.
6. Portion of mycelium from a fifty-four-day old culture of *P. lini* on oat-extract agar, showing the production of conidia on minute lateral outgrowths.
7. Portion of section through the seed-coat of an affected flax seed, showing hyphae of *P. lini* in the outer layers of cells, and two conidiophores, which have produced conidia on the surface.
8. Conidia of *P. lini* produced within an empty cell of a hypha; from a fifty-four-day old culture on oat-extract agar.

XXIII.

A NEW PRINCIPLE IN BLOWPIPE CONSTRUCTION.

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The design of a blowpipe which will be suitable for glass-blowing either in chemical and physical laboratories or on a commercial scale, is a matter which does not seem to have received the amount of attention it deserves. Though there are many forms of quick-change blowpipes in existence which are supposed to operate with great ease, none of them that have come to the writer's notice will operate really satisfactorily over the wide range of work usually required of such an instrument, even when used with a foot-bellows, and when used with a power-blower they become still less efficient.

This seems to arise from the fact, which instrument-makers appear to have overlooked, that a blowpipe which is to be used with a power-blower must be differently designed from one to be used with a foot-bellows, if it is to give satisfactory service. This oversight has led to an erroneous conclusion which is frequently seen stated, even in quite modern text-books on glass-blowing—namely, that the foot-bellows is preferable as a source of air to a power-blower, owing to the greater control it gives the worker over the flame. It is now generally conceded, however, that the power-blower enables a greater amount of work to be done with less practice, even with an ill-designed blowpipe, owing to the fact that the attention of the worker is not diverted by the working of a bellows.

It has long been the opinion of the writer that the inconvenience which arises in the use of existing types of blowpipes is due very largely to the fundamentally wrong design and construction of these instruments, and can only be remedied by bringing the design more into line with theoretical considerations.

Although the problem has been worked at from this point of view, the chief practical considerations have also been kept in view, namely, that (1) the blowpipe should give a great range of flames with the minimum of

attention from the worker; (2) it should operate satisfactorily with air at a constant pressure; and (3) it should be compact in size.

General considerations lead to the conclusion that in order to obtain flames of widely different sizes and the same character, with air at a constant low pressure, the air-jet must be variable in bore. For each size of flame there is a particular size of air-jet, which will give a well-proportioned blowpipe flame with a given air-pressure; hence one air-jet cannot be made to serve flames of different sizes satisfactorily. With blowpipes operating with a fixed air-jet and foot-bellows, this defect is partially overcome by varying the air-pressure with the size of the flame, thus supplying somewhat more air to the larger flames by more vigorous working of the bellows. Even this compromise is not quite successful, since, if the jet is of the correct bore for the smaller flames, it cannot supply enough air for the larger ones even with greatly increased pressure. When such a blowpipe is used with a power-blower, however, this difficulty becomes still greater, for it becomes necessary either to vary the speed of the motor for each change in size of flame, or to keep the motor running at the speed required for the largest flame, and vary the air-pressure by means of a tap.

It was, therefore, taken as a fundamental condition that for a blowpipe intended to work with air at a constant pressure, the air-jet must be variable in bore. The next consideration was to find a way in which this could be achieved without much difficulty. Two methods naturally suggest themselves—(1) to arrange for the actual variation of the air-jet bore by mechanical means; and (2) to provide a different-sized jet for each size of flame, and to insert each jet when using the corresponding flame.

The first method is mechanically possible, but it would involve the use of tools and processes which were not at the disposal of the writer, so that attention was mainly directed to the second method. This method is used in an existing type of blowpipe, which is usually called the "glass-blower's pattern" blowpipe, by providing a very wide air-jet, into which short pieces of capillary glass tubing can, with a certain expenditure of time and patience, be wedged with cork or paper to provide the different-sized jets.

However, it is hardly possible that this device was ever intended to be availed of in the course of work, but was rather intended to alter the blowpipe when changing from one type of work to another, since the time required to change the jet would be more than sufficient to allow the glass to cool in the course of any one operation.

The problem then narrowed down to finding a method by which the substitution of different-sized air-jets could be made extremely rapidly, with slight effort on the part of the operator, as the size of the flame varied. If

the operation of changing the jets could be "codified" so as to be performed mechanically, obviously the effect would be quite as good as an air-jet of variable bore.

Consideration of the possible ways in which this might be accomplished directed attention to the tubular shape, which is invariably seen in all types of blowpipe, and it was quickly realized that this shape, if retained, would render the design of a compact blowpipe, such as was contemplated, extremely difficult, if not impossible.

At first it was thought that the persistence of this shape in all types of blowpipe was due to the fact that it was necessary for the proper functioning of the blowpipe; but a few experiments soon showed that the tubular shape had little or no effect on the shape of the flame, and was by no means an essential feature of the blowpipe. The persistence of this shape, which only tends to make the blowpipes more unwieldy and awkward than they otherwise would be, appears to be due to the fact that the original blowpipe was made in this form, and later designers have merely modified it, without attempting any radical departure.

It was therefore decided to abandon this tubular form altogether in the design of the blowpipe to be described in this paper, and to keep the gas chamber as compact as possible, as it had been shown that this could be done without sacrificing efficiency in any way. By doing so it was found comparatively easy to design a blowpipe fulfilling the conditions which were deemed essential.

The objects aimed at in the design to be described are:—

1. To enable the change from one flame to another to be made with the minimum of attention.

2. To vary the air-supply by means of jets of different bore, the air-pressure being constant.

3. To vary the gas supply simultaneously with the air.

4. To enable any air-jet to be used with any given size of flame, in order to vary the character of the flame.

5. To make provision for a flat flame.

6. To keep the whole as compact as possible.

The principle on which the instrument is based consists in placing a number of small gas chambers (each provided with an air-jet of different bore) round the periphery of a cylinder, mounted on a horizontal axis, through which gas and air are supplied in such a way that any size of flame can be brought into operation by mere rotation of the cylinder.

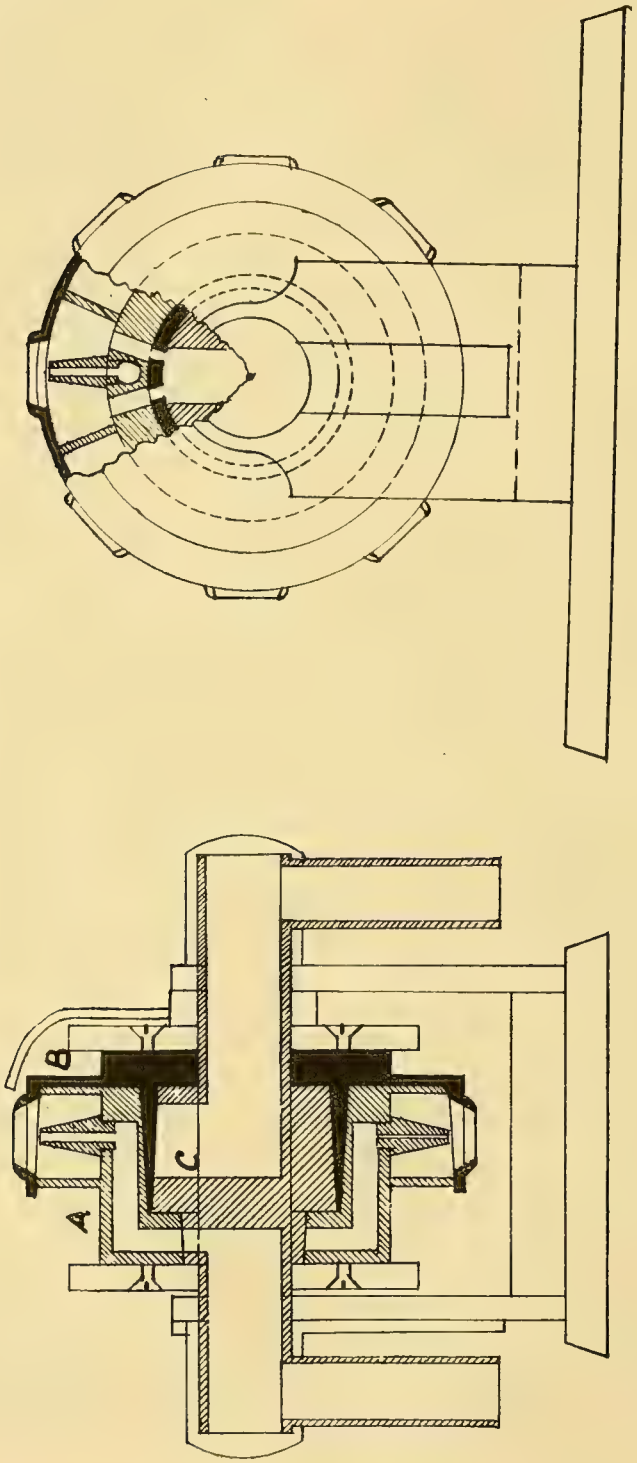

Fig. 1.

A sectional drawing of the experimental blowpipe which has been made to embody and test this principle is given in fig. 1. The instrument consists of two moving and one fixed part. The member which controls the air-supply is marked A in the drawing, and consists of a cylindrical block of brass, in which are drilled eight radial passages for the air, which communicate with eight air-jets. These air-jets are spaced equidistantly round the circumference of a deep recess formed in the brass cylinder. This recess is divided into eight equal spaces by eight brass partitions, thus forming the spaces for the gas to surround the air-jets. The gas has access to these spaces through a number of radial holes drilled in the brass cylinder, as shown in the sectional side elevation in fig. 1. The outer circumference of A is turned taper, and ground to fit the corresponding part of B, and it also has a deep conical hole bored in it for more than two-thirds of its depth, which is also ground to fit the corresponding portion of B.

The part B consists of a thin brass disc, carrying on its periphery a thin hollow cylinder, which is ground taper to fit the outer circumference of A, and is provided with eight apertures through which the flame is projected. This disc also carries a projecting portion near the centre, which has two conical surfaces, the outer fitting the conical hole in A, the inner fitting the corresponding tapered portion of C.

In this double conical portion of B there are drilled a number of equally spaced holes, which, by their size and number, vary the amount of gas admitted to the blowpipe. Two of these holes are indicated in the part-sectional side elevation (fig. 1).

The fixed portion C also consists of two oppositely tapered cones, the right hand one being tapered to fit B, and having a passage for the gas formed in it at one place, the other being tapered to fit the inner circumference of A, and provided with a passage for the air so placed as to correspond with that for the gas.

The portions A and B are free to revolve, both with respect to each other and with respect to C, but a small spring catch secures A in any desired relative position with respect to B, the two then revolving as a solid mass round C. In this way any desired air-jet on A can be brought opposite any gas-jet on B at will.

When A and B are locked together in any position, the revolution of the whole round C gives eight flames of different sizes between about one inch and twelve inches in length, and each of these flames is formed by an air-jet of just the right bore for its particular requirements; thus the bore of the largest air-jet is about ·125 inch, and that of the smallest about ·015 inch.

A by-pass is provided, which is opposite the passages bored in C, and

serves to ignite each flame as it comes into line with it by the revolution of the blowpipe. The parts A and B are provided with fibre discs with milled edges, to enable them to be easily turned when hot. The tube on which the whole is supported is held in simple trunnion bearings, and provided with a quadrant, which allows of the flame being tilted to any desired position. The gas and air are led in through short tubes which are placed at 180° to the position taken up by the flame. The whole is mounted on a simple stand of heavy metal, provided with holes for screwing to the bench.

This design of blowpipe, based as it is on theoretical considerations, naturally admits of modification and adaptation to meet particular purposes; and it will not be out of place to indicate some of the chief advantages inherent in this form.

Owing to the provision of a number of different air-jets for the different flames, the range of this blowpipe is very great, when we consider the small size of the actual working parts. The series of flames may start with a small flame about the size of that produced by a fine mouth blowpipe, and extend to a size which is limited only by the size of the blowpipe and the diameter of the gas-pipe, and yet each flame will be perfectly formed, since it is supplied with a jet of just the right size for its particular requirements. This result is obtained with gas at about four inches of water, and on air-pressure of about twelve inches of water. As well as this succession of round flames, one or more flat blowpipe flames may be produced by suitably altering the gas and air orifices.

The change from any one flame to any other is instantaneously made by mere rotation of the blowpipe on its axis, without any adjustment of taps, with the assurance that a perfect flame of the size desired will be produced in all cases. The character of the series of flames can be altered by the relative rotation of the two discs, thus producing a series of softer or harder flames according to the direction of rotation.

A further advantage is to be found in the fact that once the ratio of gas to air in any one flame is fixed (by inserting a suitable jet) the flame becomes standardized, and can be exactly reproduced at any time by using the same gas- and air-pressure. Consequently, if on one occasion any particular flame is found suitable for any operation, either in glass-blowing or general laboratory work, by noting the number of the air-jet, this flame can be reproduced easily at any future time with great precision, thus leading to the saving of time and the production of uniform results.

The principle also admits of an important development from the manufacturing point of view, inasmuch as it is possible by inserting the correct jets to arrange so that the blowpipe will give a series of flames adapted to

some particular series of operations which has to be carried out repeatedly. Thus, in making any piece of glass apparatus in quantity the same series of operations occur regularly, and the blowpipe could be arranged to give in succession the flames most suited to the different operations.

In making a small gas wash-bottle of glass, for instance, the following series of operations might occur (fig. 2):—

1. Draw out the glass tubing and seal off	large flame.
2. Round the end of large tube	medium „
3. Blow out end of large tube	very small „
4. Seal in the small tube	small „
5. Blow bulb on large tube and seal off	large „
6. Blow out pip for side tube	very small „
7. Seal on side tube	small „
8. Bend side tube to shape	large „

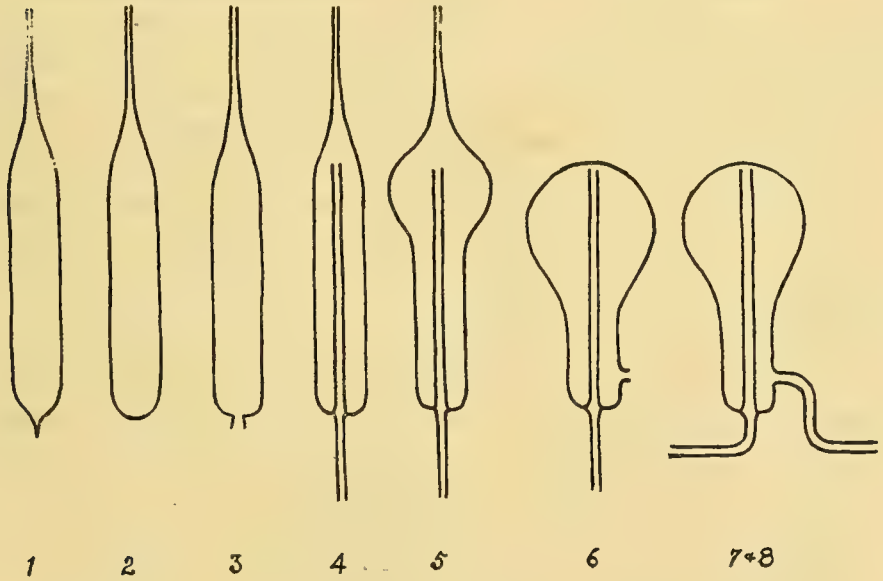

FIG. 2.

If this series of operations had to be carried out repeatedly, it would be a great saving of time to have the blowpipe so arranged that the particular flame best suited to each operation should come into operation in succession at the moment it was required.

Such an arrangement of flames could readily be obtained with the type of blowpipe described.

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XXIV.

UNCHARGED NUCLEI PRODUCED IN MOIST AIR BY ULTRA-VIOLET LIGHT AND OTHER SOURCES.

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I.—Nuclei produced by Ultra-violet Light.

Ultra-violet light acting on moist air or oxygen produces in the gas small particles or nuclei which are not electrically charged. C. T. R. Wilson, in a paper on condensation nuclei (Proc. Roy. Soc., London, **64**, p. 127), describes some experiments with these condensation nuclei, which he detected and studied by means of his expansion apparatus. When the radiation was weak, he found that the nuclei produced required as great a degree of supersaturation to cause water to condense upon them as the ions produced by X-rays, uranium, &c. With stronger radiation, however, the nuclei grew in size, requiring a smaller degree of supersaturation to produce condensation. Under favourable conditions they even became visible.

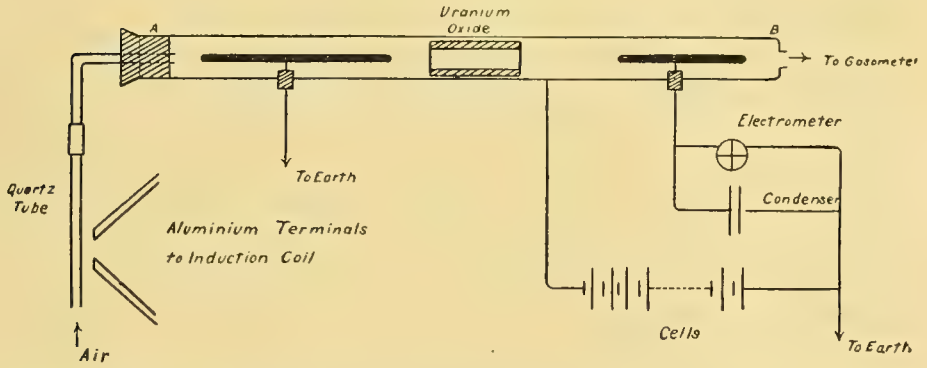
In our experiments the nuclei were detected electrically. Wilson's method of supersaturation gave but a rough idea of the size of the uncharged nuclei, and it could not be applied to dry air. In the following paper an account is given of an attempt to examine the nuclei more closely by an electrical method. Some experiments were also performed on other types of uncharged nuclei.

When uncharged nuclei pass through air ionized by uranium, X-rays, &c., they are electrified by the small ions, and thus large ions are formed, of smaller mobility, under an electric field. These large ions recombine less rapidly than the small ions; and hence, if time is allowed for the ions to recombine, the presence of nuclei originally uncharged causes an increase in the current measured.

P. Lenard and C. Ramsauer have also studied in great detail the nuclei produced by ultra-violet light. Using light of such short wave-length that it was able at once to ionize the air and to produce the nuclei, they obtained large ions, which they attributed to the combination of nuclei and ions pro-

duced separately. They quote an interesting experiment by Becker. Air was filtered and exposed to Röntgen rays, and it was found that only the ordinary small ions were produced in it. If the air, however, before being exposed to the Röntgen rays were first exposed to ultra-violet light, numerous large ions were found to be present. This leads to the conclusion that the large ions are formed by the collision of the small ions with the nuclei. It may be pointed out here, however, that the experiment is not quite conclusive, as the large ions might be produced by the photo-electric effect of the Röntgen rays on the uncharged nuclei themselves. It is shown later on in this paper that ultra-violet light, of wave-length too long to ionize the air, can cause the emission of electrons from uncharged nuclei driven off glass tubes by heating, and it might be argued that a similar process took place in Becker's experiment. Our experiments, however, in

— APPARATUS —



which ionization by the α-rays of uranium oxide took the place of the Röntgen rays of Becker's experiment, and in which positive and negative ions behaved similarly, prove conclusively that nuclei and small ions are separately produced, and by their combination with each other form the large ions.

The diagram gives a plan of our apparatus. Air was drawn by means of a gasometer through a cotton-wool plug, and then over a water surface or through drying tubes if desired. It then passed through a long quartz tube into an ionization tube containing two terminals. The first, T_1, was 50 cms. long, and generally connected to earth. The second, T_2, was 12 cms. long, and connected to a quadrant electrometer with a capacity in parallel. Between the two terminals was a glass tube which just fitted into the ionization tube, and which was coated on the inside with uranium oxide.

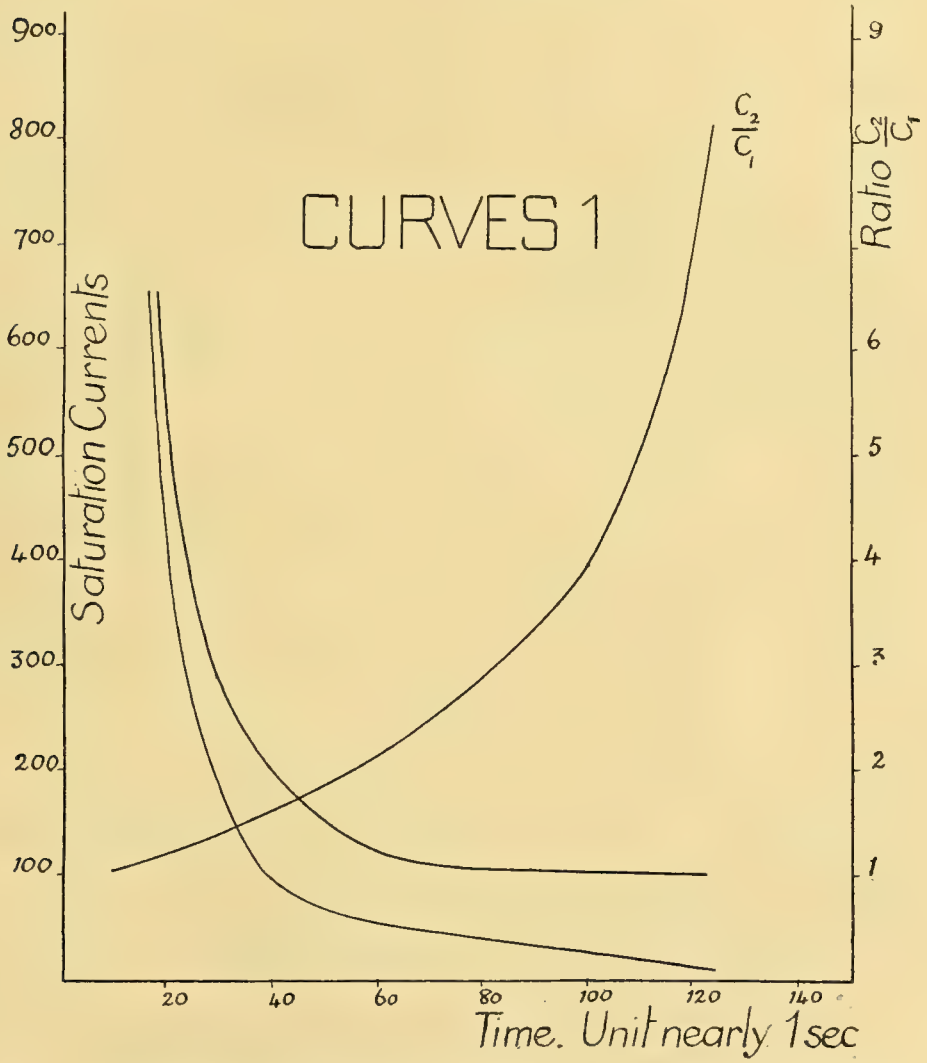
The quartz tube passed through a box lined with tinfoil and earthed. Inside the box, and opposite the quartz tube, were aluminium terminals connected to the secondary of an induction coil. The shape of the terminals enabled them to be placed, if necessary, right up against the quartz tube. A motor-driven mercury interrupter was used with the induction coil. The quartz tube was about half a millimetre thick. In most of the experiments the light also traversed 2 or 3 mms. of air.

The ultra-violet light of the spark was found, in a number of careful experiments, not to ionize the air; but as a precaution the long terminal, T_1, was used to remove to earth any ions contained in the air before its passage over the uranium oxide. The outer cylinder of the whole ionization tube AB was kept at any desired voltage by means of cells. When the air was passing through the apparatus, the ions produced by the uranium oxide took on an average about twenty or thirty seconds to reach the terminal T_2. A great number were consequently lost by recombination. The current due to the uranium oxide itself we shall call C_1. When C_1 had been measured, the spark was started. The air now passing over the uranium oxide contained the nuclei produced by the ultra-violet light. Some of these nuclei attached themselves to small ions. In this way large ions were produced which recombined less rapidly than the small ones. More ions consequently reached the terminal T_2 than when the nuclei were absent, and consequently the observed current C_2, when the spark was on, was greater than the current C_1. The current C_2 will evidently increase with the number and size of the nuclei present in the air, and thus the ratio $\frac{C_2}{C_1}$ gives an idea of the number of nuclei present. An idea as to the relative sizes of the nuclei and small ions can be got from a knowledge of their mobilities under an electric field. This mobility can be deduced from the saturation voltages in a current-voltage curve when the dimensions of the terminal and ionization tube and the quantity of air passing per second through the apparatus are known.

In our experiments, the quantity of air flowing per minute varied approximately from 1000 ccs. to 6000 ccs. The ratio $\frac{C_2}{C_1}$ varied from about 8 for slow blasts of air to about 1·2 for quick blasts. The value of the ratio $\frac{C_2}{C_1}$ is increased for slow velocities of the air through the apparatus, not only on account of the larger time allowed for recombination, but because the time of exposure of the air to the light is also increased, so that more and larger condensation nuclei are produced. For the quickest air-blasts used the nuclei had a mobility of about ·3 cms. per sec. per volt/cm.

For very slow blasts large ions were found with a mobility as low as ·00024. The slower the air-blast the smaller was the mobility.

Curves 1 represent the manner in which C_2 and C_1 decay with the time taken by the air to traverse the apparatus. The currents are, as throughout, in arbitrary units. The manner in which $\frac{C_2}{C_1}$ changes with time is also



shown. C_1, of course, is the current of small ions due to the uranium by itself when no spark is playing. C_2 is the current of large ions due to the charging by the uranium ions of the nuclei produced by the ultra-violet light. The air in all these experiments passed over a water surface. For the

quickest flow of air (7,800 ccs. per min.) the value $\frac{C_2}{C_1} = 1{\cdot}06$; for the slowest (812 ccs. per min.), $\frac{C_2}{C_1} = 8{\cdot}1$.

Mobilities met with in these Experiments.

The mobility of the charged condensation nuclei varied with the rate of flow of the air through the apparatus. The slower the rate of flow the larger were the ions. The mobilities obtained varied from ·33 to ·00024 cms. per sec. under a field of 1 volt per cm. We obtained ions of mobilities ·33, ·18, ·10, ·02, ·008, ·0044, ·0034, ·0025, and ·00024. The numbers were deduced from the saturation voltages in current-voltage curves, and do not claim a high degree of accuracy. The positive and negative ions under similar conditions have the same mobilities.

As an example of the manner in which the mobility varied with the rate of flow of the air, the following numbers will be quoted. During the experiment the intensity of the light, &c., remained constant, only the rate of flow of the air varying:—

Quantity of Air per min.	Mobility.
3600 ccs.	·18
2050 ,,	·008
1120 ,,	·0034

Effect of Varying the Intensity of the Light.

C. T. R. Wilson observed that the nuclei produced by ultra-violet light increased in size as the intensity of the light increased. Several experiments were performed by us showing that by diminishing the distance of the spark from the quartz tubes, and thus increasing the light intensity, the nuclei grew in size and became more numerous.

In these experiments, keeping the current of air constant, and a voltage on the ionization tube sufficient to "saturate" the largest ions produced, the distance of the spark was varied. One of the quartz tubes employed gave an appreciable effect up to 15 mms. distance; with the second the effect stopped at 5 mm. Thus in one experiment, calling the current due to the uranium alone, $C_1 = 100$, the following values were obtained for C_2 with

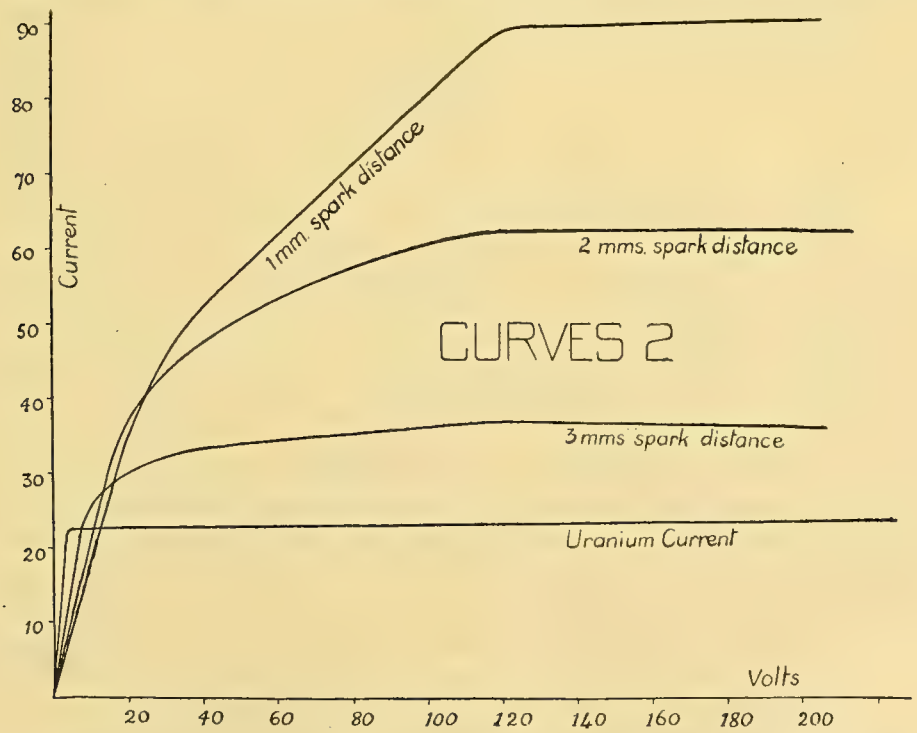
the spark at different distances, the quantity of air per minute being 2,000 ccs. :—

Distance of Spark in mms.	C_2 = current due to charged nuclei.
5	213
10	162
15	117
No Spark.	$C_1 = 100$

In another experiment, using a different quartz tube and a blast of air = 3,000 ccs. per minute, the following numbers were obtained :—

Initial uranium current, $C_1 = 236$.
Final „ „ $C_1 = 238$.

Spark distance in mms. .	= 15	10	5	3	2	1
Current C_2 . . .	= 238	250	250	365	625	910



In the latter experiment a current-voltage curve was obtained for each distance of the spark, and also one when the spark was stopped, giving the current due to the small ions alone. Curves 2 show the relative magnitude of the currents at different voltages. All the curves have the same saturation

point near 120 volts, indicating an ion of mobility about ·009. For the larger spark distances this ion is present in small quantities only. Thus when the spark is 3 mms. from the quartz tube, the largest ion is about 16 per cent. of the total; at 2 mms. 40 per cent.: at 1 mm. 61 per cent. The data from which the curves were drawn are given in the following tables :—

TABLE FOR CURVES 2.

Spark distance (mms.)	Volts.	Current.	Distance.	Volts.	Current.
No Spark	200	23·6	2 mms.	200	62·5
,,	40	22·3	,,	120	62·5
,,	20	23	,,	80	58
15 mms.	200	23·3	,,	40	47·6
10 ,,	200	25	,,	20	36·5
5 ,,	200	25	,,	10	20·8
3 mms.	200	36·5			
,,	120	37	1 mm.	200	91
,,	80	35·2	,,	120	89
,,	40	33·3	,,	80	71·4
,,	20	31·3	,,	40	52·1
,,	10	25	,,	20	35·2
			,,	10	18·5

Similar behaviour of (+) *and* (−) *Ions.*

Our experiments showed that no difference existed between positive and negative numbers; or, in other words, that the nuclei attached themselves indifferently to positive or negative small ions.

A current-voltage curve was plotted, using positive and negative voltages alternately. A preliminary test had shown that when the first terminal T_1 was earthed, and the uranium removed, no ions (due to the spark), either positive or negative, reached the second terminal T_2. The following table gives the numbers observed :—

	Voltage.	Current.
Uranium alone,	+ 120	116 (C_1)
	− 120	133 ,,
Uranium and Spark,	+ 120	833 (C_2)
	− 120	806 ,,

Ionization Curve (Uranium and Spark).

Volts positive.	Current.	Volts negative.	Current.
10	238	10	246
20	400	20	382
30	467	30	500
40	575	40	543
60	625	60	667
80	735	80	676

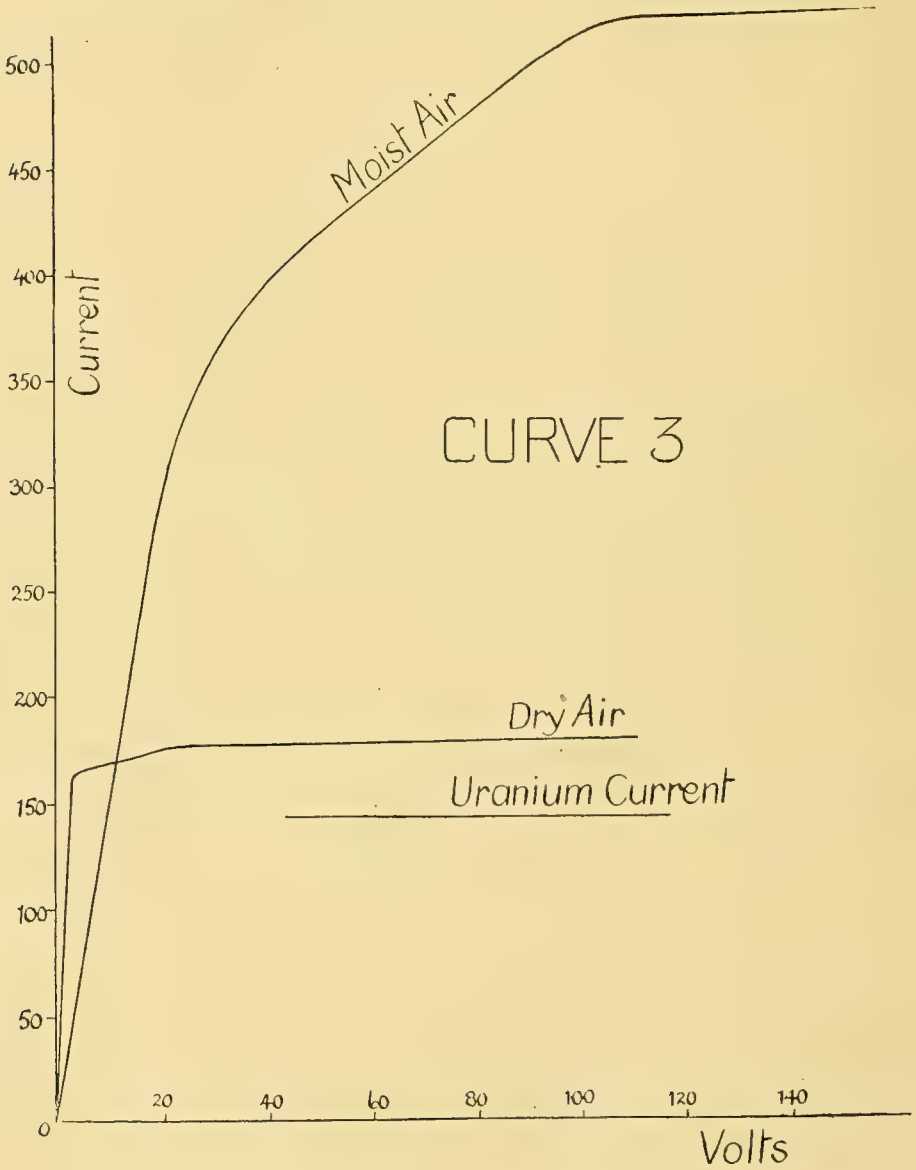
It will be evident from the tables above that positive and negative numbers are materially the same, indicating the equal behaviour of positive and negative ions.

Results similar to the preceding were obtained by Lenard and Ramsauer (*loc. cit.*). In their experiments the large ions were produced directly by Schumann—violet rays, which at once ionized the air and produced the nuclei. They found that the ions increased in size with the intensity of the light, the mobilities being measured, as in our experiments, by plotting a current-voltage curve. Increasing the time of exposure of the air to the light by diminishing the velocity of the air past the source of light also increased the size of the ions, as in our experiments. Lenard and Ramsauer give curves showing the decrease of the currents by recombination (cf. Curves 1); the rate of decrease being slower, the more vaporous impurities are contained in the air. Finally, the mobilities of the positive and negative ions were shown by them to be the same. The mobilities were deduced from the saturation points in a current-voltage curve.

Effect of Drying the Air.

The number and size of the nuclei depend upon the amount of moisture in the air. Thus the effect almost disappears in air dried by calcium chloride, but even on drying with phosphorus pentoxide a small number of nuclei seem always to be produced, as shown by a slight increase in the uranium current on switching on the spark. Curves 3 show the relative effects in moist and dry air. As will be seen, the current C_2, consisting of condensation nuclei charged by the uranium ions, is in the case of dry air only slightly greater than C_1, the current due to uranium alone, while in the case of moist air C_2 is $3\frac{1}{2}$ times as great as C_1. The saturation point in moist air is 40 volts, indicating an ion of mobility ·014. Furthermore, these ions

of mobility ·014 are nearly 50 per cent. of those formed in moist air. In dry air the largest ion is saturated at 8 volts, indicating an ion of mobility ·07, which, as is evident from the curve, forms only about 7 per cent. of the total.



In all probability rigorous drying would remove the effect altogether, but in the experiments tried by us a small number of nuclei was always formed in dry air. The effect in ordinary air depends, of course, upon the humidity of the atmosphere, but is less than the effect in air passed over a water

surface. Thus in one experiment the uranium current was increased by the spark five-fold in ordinary air, and seven-fold in air passed over a water surface. The air was filtered in both cases as usual.

Nature and Origin of the Nuclei.

It has been pointed out that the slower the moist air passed the spark the greater were the nuclei produced. If moist air at rest be exposed to strong ultra-violet light for about thirty seconds, the nuclei grow so large that they become visible, and the path of a strong beam of light through the vessel reveals a dense blue cloud, the individual particles of which can be seen in a microscope with a dark-field arrangement. Those particles are evidently drops of H_2O, and thus the nuclei which we dealt with in the preceding experiments were in all probability minute drops of water formed by the light, and growing in size with the intensity of the light and the time of exposure.

C. T. R. Wilson first attributed the formation of the nuclei to the production of some substance such as H_2O_2, which when dissolved in water lowered the equilibrium vapour-pressure, thus causing drops to be stable and grow which would otherwise evaporate. Other experimenters have proposed oxides of nitrogen as the parent substance of the nuclei.

In our experiments the difference between the formation of nuclei in dry and moist air has been shown to be very remarkable. The number and size of the nuclei were found to depend upon the quantity of water-vapour present in the air. Experimenters who used Wilson's expansion apparatus to detect the nuclei have stated that carefully dried and moist air behave similarly as to the production of nuclei (St. Sachs. Ann. der Physik, **34**, 1911, and Saltmarch, Proc. Phys. Soc., London, **27**, 1915). In view of our experiments quoted above, this must mean either that the expansion apparatus is so very sensitive a method of detecting nuclei that those formed on the slight traces of moisture left in the air after careful drying cause the formation of an appreciable cloud in the cloud-chamber, but yet would not be numerous enough to affect appreciably the value of the currents in our experiments, or else that the hygroscopic parent substance (e.g., oxides of nitrogen) is formed in dry air, and forms the large nucleus when admitted into the saturated atmosphere of the cloud-chamber. On the latter supposition, if dried air is exposed to the ultra-violet light in our experiments and then passed over a water surface before entering the ionization chamber, large nuclei should be formed and detected by the increase in the current C_2 in the usual way. This experiment was performed, but no nuclei were detected.

A further experiment was performed in which dried air was passed over a

water surface at 0°C. before being exposed to the spark. A small definite quantity of water vapour was thus contained in the air, and a small number of nuclei were formed, $\frac{C_2}{C_1}$ being found to be 1·25. On now including a second water surface at room temp. 11°C. after the quartz tube, it was thought that $\frac{C_2}{C_1}$ would increase, as if, for example, H_2O_2 were formed in the partly moist air more nuclei would be formed in passing over the second water surface. $\frac{C_2}{C_1}$ was found, however, to have the value 1·24 in this case, so that no additional nuclei were formed.

Many physicists have tried to demonstrate the presence of H_2O_2 in the nuclei formed by ultra-violet light in moist air. Vincent (Camb. Phil. Soc. Proc., 1904, **12**) used a sensitive photographic test, but failed to detect any H_2O_2. Miss Saltmarsh (*loc. cit.*) showed that prepared H_2O_2 when introduced into the expansion apparatus caused the production of nuclei. The presence of H_2O_2 in these nuclei could be demonstrated, as, when about 19 expansions were made, the showers falling into a small vessel containing titanic acid, the acid became yellow. On the other hand, 150 expansions on the nuclei produced by ultra-violet light caused no colouration of the acid. Miss Saltmarsh concluded that the part played by H_2O_2 was at most a very small one in the formation of nuclei.

On the other hand, Barkow (Ann. der Physik, **23**, 1907) found that H_2O_2 does not assist cloud-formation unless when decomposed by strong sunlight. When the H_2O_2 is exposed to strong sunlight, numerous nuclei are produced, which persist for long periods. Ultra-violet light is not necessary for this decomposition of H_2O_2, but it was not brought about by light from a strong arc lamp. Barkow tested for hydrogen peroxide in the nuclei produced by ultra-violet light in moist air by drawing them slowly through a solution containing titanic dioxide in concentrated sulphuric acid. This solution turns brown with H_2O_2, but Barkow obtained no colouration even after 150 hours, using in all 134 litres of moist air.

Barkow investigated the effect of nitrogen peroxide on the condensation of water vapour. He passed nitrogen dioxide into the cloud-chamber. Spontaneous condensation immediately took place, and many expansions were required to remove the nuclei. He also ozonized oxygen, and passed it into the expansion apparatus. The characteristic blue cloud was obtained without expansion. This spontaneous condensation with ozonized oxygen, however, Barkow attributed to the presence of small quantities of nitrogen in the oxygen used, oxides of nitrogen being formed.

Pringal (Ann. der Physik, **26**, 1908) verified the effects of oxides of nitrogen upon the condensation of water vapour, and examined Barkow's supposition that the condensation brought about by ozonized oxygen is really due to traces of nitrogen in the oxygen used. The question was a difficult one, owing to the task of obtaining oxygen entirely free from nitrogen; but Pringal set himself to examine the effect of successive purifications of the oxygen used. Oxygen prepared electrolytically was used, and after passing through the ozonizer was passed through a solution of NaOH to remove oxides of nitrogen. The spontaneous condensation still took place, and Pringal was led to believe that the ozone, even when free from oxides of nitrogen, was able to oxidize the traces of nitrogen in the cloud-chamber. Using a series of seven ozonizers, each fitted with a NaOH tube, he partially exhausted the cloud-chamber, and drew the ozonized oxygen, from which the last traces of nitrogen should have been removed, into the cloud-chamber. He repeated this process of exhaustion and replacement by ozonized oxygen, the gas in the cloud-chamber becoming freer and freer from nitrogen. The process was repeated 400 times, and the spontaneous condensation gradually decreased, and finally disappeared. Still a cloud could be formed with expansion, but even the condensation with expansion disappeared gradually. The ozonized oxygen now had no effect on the condensation of the water vapour, and the previously observed condensation was attributed to the oxides of nitrogen. Barkow and Pringal suggest that nuclei formed in moist air by ultra-violet light are similarly due to the production of oxides of nitrogen, and not to hydrogen peroxide.

In this connexion also Miss Saltmarsh examined the production of nuclei in moist nitrogen. When traces of oxygen are present nuclei are readily formed; but when the residual oxygen is removed by sparking for twenty minutes and absorbing the oxides of nitrogen in NaOH, the ultra-violet light produced no nuclei in the pure moist nitrogen.

The case for hydrogen peroxide, being the parent substance, rests upon a test by Bieber (Ann. der Physik, **39**, 1912). He passed moist oxygen exposed to ultra-violet light through a vessel at the low temperature of $-79°$ C. The condensation products were then subjected to the following tests for hydrogen peroxide :—

(1) Potass. iodide and starch, which, in the presence of ferrous sulphate, gives a blue colouration with hydrogen peroxide.

(2) Mixture of potass. ferricyanide and ferric chloride, which gives a blue colouration with H_2O_2.

(3) Dilute solution of titanium dioxide in strong sulphuric acid, which turns brown in the presence of H_2O_2.

All three tests answered for hydrogen peroxide, and the experiment is apparently conclusive. It may be objected, however, that the hydrogen peroxide detected was not present in the nuclei, but simply formed in the air by the ultra-violet light, and not affecting the condensation.

We, accordingly, tried a test in which the nuclei after being charged by uranium were driven by the field on to an electrode covered with moist paper. The paper had been dipped into a mixture of starch solution, potass. iodide, and ferrous sulphate. No blue colouration was observed even after twelve hours. The quantity of H_2O_2 may, however, have been too small to be detected by this method.

The following experiments were performed by Lenard and Ramsauer on the origin of the nuclei which were detected by their effect on the steam-jet. Air was freed from all vaporous impurities by cooling to – 76° C. No nuclei were formed in this air by ultra-violet light. Adding slight traces of water-vapour to the air caused a slight but perceptible effect on the steam-jet. Saturating the pure air with pure water-vapour by passing it over a large water surface produced a marked effect on the steam-jet, but not nearly so strong as that of ordinary moist laboratory air. It is evident, then, that water-vapour is only partially responsible for the production of the nuclei in ordinary air, and that cooling to – 76° C. removes, besides water-vapour, some other effective agent. Slight traces of water-vapour along with vapours from india-rubber gave a strong effect on the steam-jet, while the same amount of water-vapour alone, or of vapour from india-rubber alone, gave only a slight effect. We shall see later in Lenard's experiments upon other vapours, besides water-vapour in air, that ammonia gave many nuclei on exposure to ultra-violet light. It is possible that ammonia is the other effective agent besides water-vapour in ordinary air. Lenard attributes the nucleation in the case of ammonia to the formation of ammonium nitrite, and ammonium nitrate, and, where water-vapour is alone present, to the formation of hydrogen peroxide.

Experiments on Air Saturated with other Vapours.

Experiments were performed on air containing vapours of ethyl alcohol, methyl alcohol, and toluol. The room air, after being carefully dried, was passed over a surface of the liquid before being exposed to the ultra-violet light. C_1 and C_2 were then measured, as in the case of water-vapour, but in all three cases examined C_2 was equal to C_1, so that nuclei similar to those obtained with water-vapour in the air were not formed.

It was noticed in these experiments that if minute traces of either of the three vapours mentioned above were present they prevented the formation

of the nuclei in moist air. In one experiment room air was filtered and passed over a water surface and exposed to ultra-violet light. $\frac{C_2}{C_1}$ was found to be nearly 4. On putting about $\frac{1}{3}$ cc. of alcohol in the water, whose volume was about 1,000 ccs., $\frac{C_2}{C_1}$ dropped to the value unity, so that no nuclei were formed.

The action of the alcohol-vapour in preventing the formation of the nuclei might be in either of two ways. It might prevent the formation of the hygroscopic substance (e.g., H_2O_2) which is the parent of the nucleus, or it might act on the minute water-drops after formation.

To test this point, nuclei were produced in moist air and then passed over an alcohol surface. After passing over the alcohol surface the nuclei could no longer be detected by our methods, the action of the alcohol-vapour being just the same as if it had been contained in the air before exposure to the ultra-violet light.

Air saturated with alcohol-vapour was now exposed to intense ultra-violet light in a closed vessel for some time. A narrow beam of intense arc light traversed the vessel. Its path was at first invisible, but when the spark had acted for thirty seconds or so a thin cloud of large drops was seen in the beam. Using water instead of alcohol, and exposing for the same time, a cloud is also formed, but very different in appearance. It is now blue, the arc light appearing as a solid blue beam through the vessel. The drops in the case of water-vapour are evidently much smaller and more numerous than when alcohol-vapour is used.

The effect of adding traces of alcohol-vapour to the water-vapour in the above experiment is to prevent the formation of the characteristic blue cloud. A thin cloud of large drops is, however, formed similar to that obtained with alcohol-vapour alone. In the light of these results the reason why no nuclei were detected in our experiments by the electrical method is that, although nuclei were formed, they grew so big and were so few that their presence could not be demonstrated by our methods.

Lenard and Ramsauer also investigated other vapours besides water. Alcohol, methyl, ether, benzol, chloroform, atrachinon, and alizarin were found to be ineffective. Benzine was slightly effective in forming nuclei. Ammonia, hydrogen bi-sulphide, carbon-disulphide were effective. In these experiments pure air was passed over a bulb containing water, and another containing the liquid to be examined. In addition, Lenard examined the nuclei formation in moist gases other than air. Oxygen and carbon-dioxide behaved like air; but no nuclei were formed in moist hydrogen. No nuclei were formed in water-vapour alone.

II.—Nuclei driven off Glass Tubes by Heat.

If a glass tube be heated while air is passing through it, uncharged particles are given off which can be charged by passing over uranium oxide. The apparatus previously described was used also in these experiments, the glass tube examined being included between the cotton-wool filter and the quartz tube. A small quantity of charged particles was also given off when a tube was heated.

The tube was generally heated with a luminous gas flame extending over about an inch of the tube. The presence of the nuclei was demonstrated by an increase in the uranium current just as described in the case of the nuclei produced in moist air by ultra-violet light. The emission of the nuclei fell off rapidly, almost ceasing in about ten minutes generally, the current registered falling off to the value of the uranium current alone. The effect reappeared, however, on heating a cool place on the tube.

Thus in one experiment the following numbers were obtained :—

Small ion current (uranium alone) . .	$C_1 = 19{\cdot}8$
Current of nuclei driven by heat from glass and charged by the uranium ions . .	$C_2 = 90{\cdot}9$
After ten minutes' heating . . .	$C_2 = 20{\cdot}8$

The large increase in the current would lead us to expect that the nuclei are of great size. An attempt was then made to plot a current voltage curve. Owing to the fatigue effect it was necessary for each reading to heat a new place of the tube, beginning at that part furthest from the end where the air entered. The charged ions driven off the tube by heat were removed to earth by a second ionization tube as above described, so that the total increase in the current is due to the uncharged nuclei. Saturation occurred at 280 volts, giving a mobility of ·0044. The curve also indicated the presence of a smaller ion of mobility about ·016. The mobility ·0048 was obtained in another experiment.

Another experiment on a different tube did not give saturation at 400 volts—the highest voltage then available. This indicated an ion of mobility less than ·0028. The experiment was repeated, using a longer terminal, and the mobility ·0016 obtained.

The nuclei obtained by heating glass tubes are much more numerous than those produced by ultra-violet light in moist air. In the latter experiments some indications were always found of unattached small ions, whereas the nuclei driven off by heat from glass tubes were so numerous that every small ion attached itself to a nucleus before reaching the terminal.

The tubes which lost on heating the property of emitting uncharged

nuclei regained that property after a certain interval and under certain conditions. The following experiments will be quoted as examples.

A glass tube was strongly heated in a Bunsen flame and "fatigued." It was left open, exposed to the atmosphere for a few days. When again examined it had recovered, the ratio $\frac{C_2}{C_1}$ being almost as great as when the tube was fresh. Heating for fifteen minutes suffices to drive off nearly all the nuclei, the value of $\frac{C_2}{C_1}$ falling off almost to unity.

It might be expected that the effect would be recovered immediately on cooling. This is not the case, nor is the effect recovered if the tube is left in the apparatus overnight closed in. Thus several glass tubes which had been fatigued were found not to recover if left for several days in the apparatus closed in, but recovered fully if left overnight fully exposed to the atmosphere.

The nuclei driven off by heat from glass tubes can also be charged by exposure to ultra-violet light. The apparatus is in this case identical with that described in the previous experiments. The uranium is, of course, excluded. The tube is heated, and the nuclei so obtained are exposed during their passage through the quartz tube to the ultra-violet light of the spark, which is a few mms. distant. A current voltage curve for the positive ions thus obtained gave a mobility of ·0009.

When a tube is heated and fatigued, as above described, the nuclei which can be charged by passing over uranium are recovered in about twenty-four hours when the tube is exposed to the atmosphere. The property of emitting nuclei, which could be charged by ultra-violet light, is not regained so rapidly. Thus a tube which recovered in twenty-four hours the property of emitting nuclei which were charged by the uranium small ions gave off no nuclei which could be charged by ultra-violet light. The latter property, however, it regained in about a week. It may be that the nuclei are not acted upon by ultra-violet light until they reach a certain size, and that in the initial stages of recovery of a glass tube the nuclei given off are small.

The ultra-violet effect is probably due to the photo-electric emissions of electrons from rather big particles. If this is the case, we should expect that many of the electrons would be lost by diffusion to the sides of the vessel before becoming attached to neutral particles. We should thus expect the positive numbers to be greater than the negative.

An experiment was performed with a new glass tube to investigate this point. Positive and negative numbers were taken alternately, the spark running continuously, and the tube heated for each reading at a different

place. The negative numbers were very small compared with the positive the rate of flow of the air being slow (1200 ccs. per min.). The saturation current was ten times as great for positive as for negative numbers. The positive ions were saturated between 320 and 400 volts, giving a mobility between ·0015 and ·0012. The negative ions had a lower saturation point, and were thus smaller than the positive. The numbers obtained are shown in the following table:—

Currents obtained on heating glass tube and charging nuclei by ultra-violet light.

Volts (+)	Current (+)	Volts (−)	Current (−)
80	50	80	13·3
160	100	160	20·4
240	139	240	22·7
320	200	320	21·7
400	227		
440	192		

On the other hand, as might be expected, it was proved in many experiments that when nuclei are driven from a glass tube by heat and passed over uranium, the resulting numbers, positive and negative, are equal, any charged products from the glass tube being previously removed to earth, as in our other experiments.

It was thought possible that passing dry air through the glass tube would remove the matter which gives rise to the condensation nuclei driven off by heat. A glass tube, however, through which dry air had passed for several hours was unchanged, and gave the same effect as before the drying. Whether the air drawn through the glass tube while heated is dry or moist makes no difference in the numbers of nuclei emitted.

In dealing with soft glass tubes a second type of nuclei emission was encountered with stronger heating. If a soft glass tube be heated with a luminous flame, the emission falls off almost to zero in ten or fifteen minutes. If the fatigued part be now heated with a strong Bunsen flame, the emission is very much increased, and remains constant for a long time, no sign of fatigue being observed. In this second case the glass tube glows, and the nuclei are due probably to the decomposition of the glass itself.

III.—Nuclei driven off from Metals by Heat.

A series of experiments were conducted on the nuclei driven off by heat from a platinum wire electrically heated. The platinum wire used was thin, having a resistance per cm. of about ·15 ohms. The air after being filtered and, if necessary, dried, passed through a wide glass tube. Through corks in the ends of the tube thick copper wires were introduced supporting about 5 cms. of the platinum wire. A variable resistance and a sensitive ammeter completed the heating circuit. The wide glass tube containing the platinum wire was heated strongly in a Bunsen flame before being used, to expel all the nuclei from the glass. This precaution was, perhaps, unnecessary owing to the width of the glass tubes, whose diameter was about 6 cms., and which did not become very hot in the experiments.

The remainder of the apparatus was similar to that used in the experiments on nuclei produced by ultra-violet light. The nuclei emitted by the platinum wire were passed over a long terminal connected to earth, then over uranium, and were detected at the short terminal connected to the electrometer. The mobility of the nuclei when charged was deduced from a current-voltage curve as before, and gave an idea of their size.

For simplicity, we shall first deal with the nuclei emitted when the wire has been kept for some time at a dull red heat. The emission then becomes very steady, and seems to be a function of the temperature alone, so that when the velocity of the air through the apparatus remains constant the number and size of the nuclei depend solely upon the current through the wire. For example, if the emission is measured at a given temperature, and the wire be kept then at a much higher temperature even for hours, on decreasing the temperature of the wire to its former value the emission of the nuclei as deducted from the ratio $\frac{C_2}{C_1}$ is found to be unaltered.

It was thought that the nuclei might have been formed by some catalytic action of the platinum upon the moist air, in which the platinum itself was unchanged. Whether the air was moist, however, or carefully dried over calcium chloride and phosphorus pentoxide made not the slightest difference in the numbers. The nuclei were, therefore, due in all probability to the disintegration of the platinum itself.

The size of the nuclei increased with the temperature of the wire. $\frac{C_2}{C_1}$ was measured for currents of 1·2, 1·3, and 1·5 amperes through the wire, the air velocity through the apparatus remaining constant. A current-

voltage curve was plotted for C_2, and the mobilities deduced from the saturation voltages. The results are seen in the following table :—

Current through wire.	$\frac{C_2}{C_1}$	Saturation Voltage (C_2).	Mobility.
1·2	2·5	70	·013
1·3	7·2	120	·008
1·5	> 9·6	> 400	< ·0022

When 1·5 amperes were used saturation did not occur even at 400 volts, the highest voltage obtainable at the time. The numbers, however, show clearly how the size of the nuclei depends upon the temperature of the wire.

In observing the emission from platinum at a given temperature, no falling-off is observed even after hours; but if the same wire is heated from day to day, a gradual falling-off is observed, although as long as the wire is glowing nuclei are always emitted in large numbers.

In addition to the nuclei given off by platinum when glowing, nuclei are also emitted at lower temperatures by fresh wires, but the effect falls off rapidly to zero, and is thus not easily detected. A fresh wire was heated by currents from ·5 ampere up, and the values of C_1 and C_2 taken at each reading of the current. No nuclei were observed at ·5 amp. nor at ·8 amp.; but when the current was 1·0 amp., C_2 was originally four times C_1, but rapidly fell off to a value near C_1, showing that the emission of nuclei fell off to zero. The wire just began to glow at 1·1 amps., and at that low temperature, although the emission never fell off to zero, the wire, when fresh, emitted more nuclei than after it had been heated for some time.

Taking another new piece of wire, the following values of C_1 and C_2 were got for the given currents through the wire. C_1 and C_2 are given in arbitrary units :—

C_1	16
C_2 at 0·5 Amp. . .	16
,, at 0·8 ,, . .	53
Successive readings at 0·8 ,, . .	20
,, ,, at 0·8 ,, . .	15

Thus a large number of nuclei were emitted when 0·8 ampere passed through the wire. Three readings, each taking about one minute, were made

of C_2. The numbers show that the emission fell off to zero in about three minutes.

On increasing the current to 1·0 ampere more nuclei were emitted (although the wire was not glowing). The emission in this case also fell off almost to zero, but took a much longer time than that at ·8 amp. The following values of C_2 and C_1 were got at 1·0 ampere :—

C_1 =	14·5
C_2 (1st Reading)	52·6
,, (2nd ,,)	33·3
,, (3rd ,,)	28·6
,, (4th ,,)	24·4
,, (5th ,,	23·3
C_1 again	14·5

It will be seen that the rate of emission gradually decreased, but even after about five minutes was still appreciable. On leaving the current at 1·0 amp. for thirty minutes, C_2 was found to be 15·4 and C_1 14·0, so that the emission of nuclei had practically ceased.

On increasing the current through the wire to 1·2 amperes the wire glowed, and C_2 was 37, while C_1 was 15·3. The same values were obtained after twenty minutes' heating.

The initial emission at 0·8 and 1·0 amperes was not regained by the wire even on being laid aside for over three weeks. It is probably due to the emission of occluded substances in the platinum or to surface impurities received, for example, in handling. A fresh platinum wire which was heated in a Bunsen flame before being examined as above did not emit any nuclei at the temperatures corresponding to 0·8 and 1·0 amperes.

With a wire made of ni-chrome, an alloy of nickel and chromium, results were obtained similar to those described for platinum. The wire in this case began to glow at a current of about 3 amps., but nuclei were emitted from the fresh wire at 1·5 amperes. This initial emission rapidly fell off to zero.

The emission at glowing temperatures remained constant for hours, but in using one wire from day to day a marked falling-off is observed. This was clearly shown by the values at 4·0 amps. of $\frac{C_2}{C_1}$, which fell in about a week from the value 5·4 to 2·5, 1·4, 1·25, and finally 1·2.

SUMMARY.

I.

The nuclei produced by ultra-violet light in moist air are detected by an electrical method, and their size indicated by their mobility, when charged in an electrical field. The number and size of the nuclei depend upon the time of exposure to the light, the intensity of the light, and the amount of moisture in the air.

The nuclei are probably small water-drops which owe their formation to the production in the moist air by ultra-violet light of some hygroscopic substance, such as hydrogen peroxide or oxides of nitrogen. An account of work by other experimenters is given, and the evidence, though not conclusive, points to hydrogen peroxide as the parent substance of the nucleus.

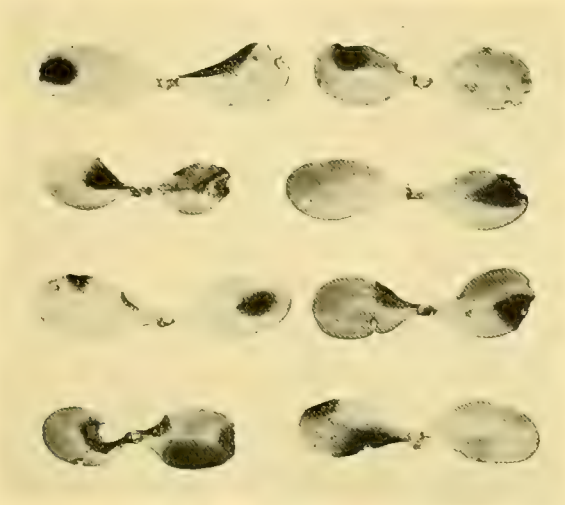
Some experiments were performed in air containing, instead of water, the vapours of methyl alcohol, ethyl alcohol, and toluene respectively. No nuclei are found by our method, probably because the nuclei grow so big, and decrease so much in number, that they fail to affect the currents in our apparatus. The presence of very slight traces of either of these vapours in water-vapour prevents the formation of nuclei such as can be detected by our apparatus, and probably for the same reason.

II.

The nuclei which are emitted by a glass tube when heated not too strongly can be detected and measured in a manner similar to that described for the nuclei produced by ultra-violet light. The emission of nuclei when the heating is not too strong lasts only a few minutes, but the tube "recovers" under certain conditions.

The nuclei can be charged by ultra-violet light, probably by the photo-electric discharge of electrons from the rather large particles. The positive ions are found to be much more numerous and of much greater size than the negative. In all probability only particles greater than a certain size are acted on by the light. The electrons then become attached to the smaller particles or the air molecules. The negative ions thus formed are numerically more decreased by diffusion to the walls of the apparatus than the larger positive ions.

The experiments on the recovery of glass tubes fatigued by heat seem to indicate a difference between those nuclei which can be charged by ultra-violet light and those which can be charged by the small ions produced by



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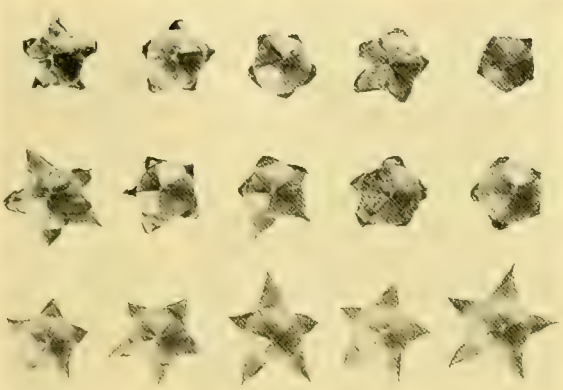

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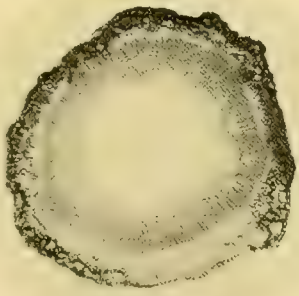

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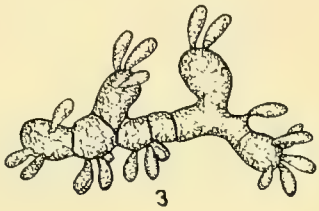

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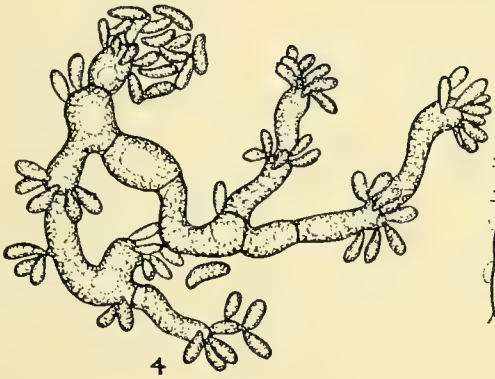

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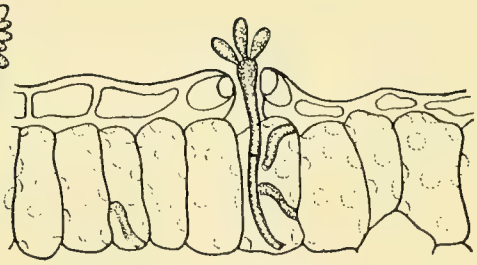

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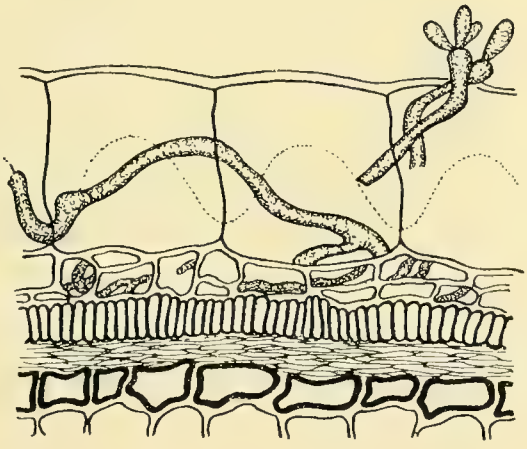

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uranium. The difference is probably, however, one of size, as in the initial stages of recovery the particles emitted may not be so large as they become after a prolonged period of rest.

Nuclei of a different type are emitted at glowing temperatures. In this case the glass does not become fatigued, and the nuclei are probably produced by the decomposition of the glass itself.

III.

When platinum wires are heated electrically, nuclei are driven off before the wire begins to glow. This emission lasts only a short time, just as in the case of glass, and is probably due to occluded impurities.

When these impurities are driven off by heat, the wire emits no nuclei until it begins to glow. The emission at glowing temperatures is very constant, and does not fatigue. The size and number of the nuclei emitted increase with the temperature.

Similar results were obtained with a wire of ni-chrome, an alloy of nickel and chromium.

Thus in all cases examined where nuclei are driven off from a substance by heat an initial emission takes place at low temperatures which falls off rapidly. The emission of nuclei when the substance glows is practically constant.

XXV.

BIOLOGICAL STUDIES OF *APHIS RUMICIS* L.

A.—Appearance of Winged Forms.
B.—Appearance of Sexual Forms.

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(communicated by professor G. H. carpenter.)

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I.—Introduction and Experimental Data.

The results embodied in this paper have been derived from extensive breeding experiments with this species in captivity during 1913-14 in Germany and 1920 at Rothamsted. Ova were found on March 25th, 1914, and were hatched out in the laboratory, the Fundatrices being transferred to small *Euonymus* bushes, *Rumex* plants, etc., which were grown in pots, and kept covered with muslin bags. As each succeeding generation became adult, some of the offspring were transferred to new plants. In this way the history of the aphids used was known, and the exact generation with which the various plants were infected. Unfortunately, for the 1920 experiments ova could not be found, so that the colonies in these experiments were started from an early, viviparous, parthenogenetic generation found on *Euonymus europaeus* on the Rothamsted farm on May 10th, 1920.

The plants were grown in 10″ pots in a large open glass-house in summer, and a warm green-house in winter. The daily maximum and minimum temperature of the green-house throughout the winter is shown in fig. 2.

I wish to express my thanks to Dr. A. D. Imms for the helpful suggestions he has given me during the progress of the experiments, and to Mr. Ward Cutler for his criticism when writing the paper.

(a) *Fundatrix Generation on Euonymus.*

Young aphids (1st instar), which hatched out from ova of *Aphis rumicis*, from *Euonymus*, were reared on young twigs of *Euonymus europaeus*, which were kept in wet sand in the laboratory. They all developed into a.v. ♀ ♀, being the adult Fundatrices.

In six experiments it was found that Fundatrices became adult in 8 to 10 days after birth, and commenced to produce young within 2 to 4 days after the last moult. The young in all cases were apterous viviparous females.

(b) *The First Viviparous Generation on Euonymus europaeus.*

The offspring of the Fundatrices are the first viviparous generation. In these experiments, individuals of the first viviparous generation born between April 13th and 18th, 1914, became adult in 9–11 days after birth. In all cases they gave rise to a.v. ♀ ♀, and the first young were produced in seven instances on the same day that the last moult took place. In the remaining cases, the first young were produced in 1 to 3 days after the last moult. They were grown on twigs of *Euonymus* in wet sand.

(c) *Successive Viviparous Generation reared on Euonymus.*

Small *Euonymus* bushes, about a foot high, were grown in pots and infected as required, each plant being covered with a muslin bag. Observations were made as recorded below. It should be noted that when winged forms are transferred to a new plant there is often great difficulty in getting them to settle down on the plant, and several days may elapse before they produce young on it. Sometimes, out of as many as fifteen winged forms, only two or three will settle down and produce on the plant, the remainder collecting in the top of the muslin cover. By restricting the space round the plant, this difficulty can be somewhat overcome.

Euonymus A.—11. 4. 14. Infected with two Fundatrices reared from ova on Euonymus. 23. 4. 14. Adult w. v. ♀ ♀ present; only a few a. v. ♀ ♀ present.

Euonymus A_1.—23. 4. 14. Infected with 4 w. v. ♀ ♀, 1st v. gen. from A. 12. 5. 14. Plant is not making young growth and is "woody." Aphids small size, restless, and wandering over the plant; some immature w. v. ♀ ♀ present, but majority are a. v. ♀ ♀, some a. v. ♀ ♀ adult.

Euonymus A_2.—25. 4. 14. Infected with 3 w. v. ♀ ♀, 1st v. gen. from A.

8. 5. 14. 2nd v. gen. are all a. v. ♀ ♀, large size, dull black in colour, with parts of legs and antennae yellowish white in contrast; the plant making young growth. 24. 5. 14. Plant heavily infested, aphids small size, many w. v. ♀ ♀ present.

Euonymus A_3.—27. 4. 14. Infected with 2 a. v. ♀ ♀, 1st v. gen. from A. 18. 5. 14. Plant is not making young growth; aphids small size; majority are w. v. ♀ ♀, only 3 a. v. ♀ ♀ present.

Euonymus A_4.—12. 5. 14. Infected with 5 a. v. ♀ ♀, 2nd v. gen. from A_1. 24. 5. 14. 3rd v. gen. are a. v. ♀ ♀ and w. v. ♀ ♀.

Euonymus A_5.—10. 5. 14. Infected with 3 a. v. ♀ ♀, 2nd v. gen. from A_2. 24. 5. 14. 3rd v. gen. practically all w. v. ♀ ♀; plant has young growth.

Euonymus A_6.—24. 5. 14. Infected with 4 w. v. ♀ ♀, 3rd v. gen. from A_5. 10. 6. 14. 4th v. gen. small numbers but large size, all a. v. ♀ ♀, some adult.

Euonymus A_7.—10. 6. 14. Infected with 8 a. v. ♀ ♀, 4th v. gen. from A_6. 20. 6. 14. Some aphids of 5th v. gen. are adult; all are w. v. ♀ ♀; plant has young growth.

Euonymus A_8.—20. 6. 14. Infected with 6 w. v. ♀ ♀, 5th v. gen. from A_7. 26. 6. 14. All the w. v. ♀ ♀ have died without producing any young. Reinfected with 8 w. v. ♀ ♀ from A_7. 6. 7. 14. About 20 aphids 6th v. gen. produced; killed off the winged mothers. 15. 7. 14. 6th v. gen. not yet adult; very small size; plant not making young growth; transferred the aphids to a new plant. 23. 7. 14. Some of the aphids now adult; all are a. v. ♀ ♀ small size; plant is not making young growth. 30. 7. 14. Aphids very small size; plant woody; several aphids of 7th v. gen. produced.

Owing to the unavoidable termination of the "A" series in July, 1914, the experiments were continued during the summer of 1920. As it was not possible to find ova of *Aphis rumicis*, the experiments were started with an early apterous viviparous generation found on *Euonymus europaeus* on 10th May, 1920. Winged forms were present, so it might be presumed that these were probably the second viviparous generation after Fundatrices. Allowing ten days for development of each generation, this would mean that the eggs hatched about April 10th.

Small *Euonymus* trees grown in pots and covered with muslin bags were infected as recorded below. By "cutting back" the bushes, young growth was obtained throughout the summer.

Euonymus E_1.—10. 5. 20. Infected with two a. v. ♀ ♀ from Euonymus europaeus. 15. 7. 20. Plant heavily infested.

Euonymus E_2.—15. 7. 20. Infected with 8 a. v. ♀ ♀ from Euonymus E_1. 28. 7. 20. About 30 aphids produced, big and healthy; plant has young growth. 10. 8. 20. Many winged forms produced; a few ♂ ♂ present.

Euonymus E_3.—18. 8. 20. Infected with a. v. ♀ ♀ and winged forms from Euonymus E_2. 24. 8. 20. A. v. ♀ ♀ producing young; only one winged form producing, remainder will not settle on the plant. 31. 8. 20. Only a few Aphids on the plant, small size, apterous. 14. 10. 20. The plant is shedding its leaves; a good number of aphids present; small size; many winged forms; ♂ ♂ and sexual ♀ ♀ present.

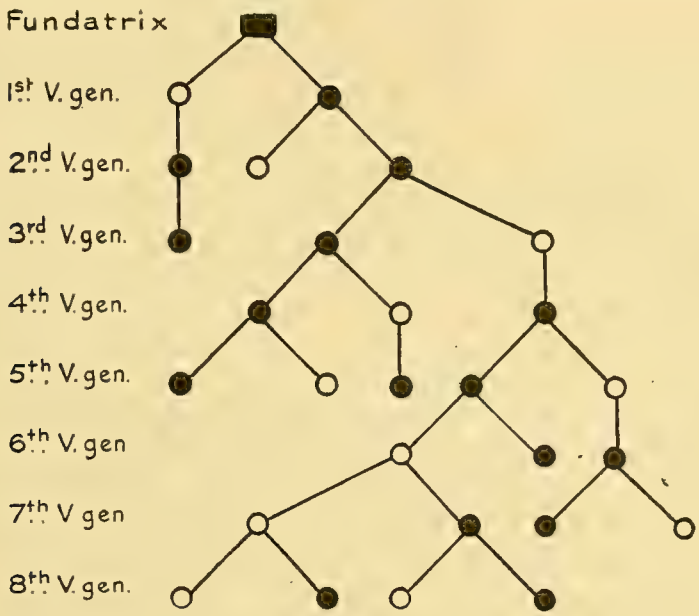

FIG. 1.

Table illustrating appearance of winged and apterous forms of Aphis rumicis on Rumex. 1st v. gen., etc., = 1st viviparous generation; ● = a.v. ♀ ♀; O = w.v. ♀ ♀.

(d) *Successive Viviparous Generations reared on Rumex.*

Rumex plants were grown in pots and infected with a. v. ♀ ♀ and w. v. ♀ ♀ respectively, in the different generations.

The first infection was to Rumex No. 1 with one Fundatrix of *Aphis rumicis* from *Euonymus europaeus* on 13. 4. 14.

The last infections were Rumex Nos. 16 and 17 with w. v. ♀ ♀ and a. v. ♀ ♀ respectively, of the 7th v. gen. from Rumex No. 14 on 16. 7. 14.

The aphids made rapid progress, and were usually of large size and dull olive green colour.

In some generations only apterous forms were produced, although winged forms always appeared in later generations, when the aphids were left to reproduce on the plant.

The appearance of the winged and apterous forms is shown in fig. 1.

It must be noted, however, that, owing to technical difficulties, where so many breeding cages are under observation, it is not possible to breed out all the offspring. The table below must therefore be taken as only expressing the general trend of the appearance of winged and apterous viviparous females.

(e) *Successive Generations of Aphis rumicis on Broad Beans.*

(Variety: Sutton's Prolific Longpod.)

Broad Beans B.—16. 6. 20. Infected with 2 a. v. ♀ ♀; offspring of winged migrants on Broad Beans. 12. 7. 20. A large number of aphids present, a. v. ♀ ♀ and w. v. ♀ ♀.

Broad Beans B_1.—10. 7. 20. Infected with 4 a. v. ♀ ♀ from B. 19. 7. 20. Offspring adult. 26. 7. 20. One adult w. v. ♀ ♀, remainder a. v. ♀ ♀, large size, infestation heavy; killed off the plant and infected a new plant with four of the a. v. ♀ ♀. 10. 8. 20. Many a. v. ♀ ♀ and w. v. ♀ ♀ present.

Broad Beans B_2.—10. 7. 20. Infected with 4 w. v. ♀ ♀ from B. 19. 7. 20. Some a. v. ♀ ♀ adult, large size. 26. 7. 20. Infestation heavy.

Broad Beans B_3.—25. 7. 20. Infected with 6 a. v ♀ ♀ from B_2. 4. 8. 20. A. v. ♀ ♀ and w. v. ♀ ♀ present. 12. 8. 20. Many winged forms present.

Broad Beans B_4.—6. 8. 20. Infected with 6 a. v. ♀ ♀ from B_3. 27. 8. 20. Infestation heavy, a. v. ♀ ♀ and w. v. ♀ ♀ present; killed off plant and infected a new plant with some of the apterous and winged forms. 14. 9. 20. Many a. v. ♀ ♀ and w. v. ♀ ♀ present; killed off the new plant.

Broad Beans B_5.—14. 9. 20. Infected with 5 a. v. ♀ ♀ from B_4. 11. 10. 20. A. v. ♀ ♀; w. v. ♀ ♀, a few ♂ ♂, and two sexual ♀ ♀ present.

Broad Beans B_6.—11. 10. 20. Infected with 10 a. v. ♀ ♀ from B_5. 29. 10. 20. A few a. v. ♀ ♀, many w. v. ♀ ♀, and several ♂ ♂ present. Development slow owing to low temperature in glass-house.

NOTE.—From B_7 onwards the plants were kept in a warm green-house, the temperature varying as shown in chart, text (fig. 2).

Broad Beans B_7.—29. 10. 20. Infected with 5 a. v. ♀ ♀ from B_6. 18. 11. 20. 3 w. v. ♀ ♀ adult, many immature winged forms, large size (sexuparae alatae). 26. 11. 20. All the aphids are w. v. ♀ ♀ (sexuparae), and a few ♂ ♂.

Broad Beans B_8.—23. 11. 20. Infected with one of the a. v. ♀ mothers on B_7. 5. 12. 20. Four w. v. ♀ ♀ and one a. v. ♀ produced. Allowed w. v. ♀ ♀ to produce on the same plant. 26. 12. 20. The w. v. ♀ ♀ have produced oviparous ♀ ♀.

Broad Beans B_9.—(Two plants.) Infected one plant on 19. 11. 20, and the other on 25. 11. 20, each with one w. v. ♀ from B_7. Only sexual ♀ ♀ produced in each case; hence these are true female-producing sexuparae.

They produced 11 and 22 females respectively, which were adult on 5. 12. 20 and 9. 12. 20. A third w. v. ♀ produced only sexual ♀ ♀.

Broad Beans B_{10}.—5. 12. 20. Infected with a. v. ♀ from B_8. 23. 12. 20. One a. v. ♀ produced, remainder are w. v. ♀ ♀; total 20.

Broad Beans B_{11}.—1. 12. 20. Infected with 10 w. v. ♀ ♀ from B_7. 26. 12. 20. All the aphids produced are sexual ♀ ♀.

Broad Beans B_{12}.—23. 12. 20. Infected with the one a. v. ♀ from B_{10}. 9. 1. 21. Offspring consists of 10 w. v. ♀ ♀ adult, 2 adult a. v. ♀ ♀, and remainder nymphs of winged forms; some ♂ ♂.

Broad Beans B_{13}.—26. 12. 20. Infected with 10 w. v. ♀ ♀ from B_{10}. 1. 1. 21. Four w. v. ♀ ♀ have produced young. 12. 1. 21. All offspring are oviparous ♀ ♀; some are adult.

Broad Beans B_{14}.—10. 1. 21. Infected with 2 a. v. ♀ ♀ from B_{12}. 5. 2. 21. w. v. ♀ ♀ (sexuparae), ♂ ♂, and 4 a. v. ♀ ♀ produced.

Broad Beans B_{15}—10. 1. 21. Infected with 5 w. v. ♀ ♀ from B_{12}. 24. 1. 21. 18 oviparous ♀ ♀ produced.

Broad Beans B_{16}.—24. 1. 21. Infected with 4 a. v. ♀ ♀ from B_{14}. 3. 2. 21. 3 ♂ ♂; several w. v. ♀ ♀ and 1 a. v. ♀ produced.

Broad Beans B_{17}.—5. 2. 21. Infected with 5 w. v. ♀ ♀ from B_{14}. 21. 2. 21. Only one w. v. ♀ reproduced, and gave 6 oviparous ♀ ♀.

Broad Beans B_{18}.—3. 2. 21. Infected with the 5 a. v. ♀ ♀ from B_{16}. 23. 2. 21. 2 a. v. ♀ ♀; several ♂ ♂; several w. v. ♀ ♀ present. 19. 2. 21. The 5 original a. v. ♀ mothers put on a new plant, and on 2. 3. 21 they had produced 3 a. v. ♀ ♀, some ♂ ♂, and w. v. ♀ ♀.

Broad Beans B_{19}.—23. 2. 21. Infected with 5 w. v. ♀ ♀ from B_{18}. 10. 3. 21. All oviparous ♀ ♀ produced.

Broad Beans B_{20}.—2. 3. 21. Three plants infected each with one a. v. ♀ from B_{18}. 26. 3. 21. 5 a. v. ♀ ♀, one ♂, and 40 w. v. ♀ ♀ produced.

(f) *Euonymus Europaeus Infected from Broad Beans.*

Euonymus E_6.—16. 6. 20. Infected with a. v. ♀ ♀, offspring of winged migrants on Broad Beans. 29. 6. 20. Many aphids present, mostly a. v. ♀ ♀, but some w. v. ♀ ♀.

Euonymus E_7.—10. 7. 20. Infected with 25 w. v. ♀ ♀ from Beans B. 18. 7. 20. Many colonies produced beneath the leaves. 5. 8. 20. Aphids small size, dark colour, many winged forms; infestation heavy; plant has no young growth.

Euonymus E_8.—19. 8. 20. Infected with 15 w. v. ♀ ♀ from Beans B_4. 31. 8. 20. Many aphids produced, some adult a. v. ♀ ♀ 14. 9. 20. Plant heavily infested; many aphids wandering over the plant and muslin cover.

14. 10. 20. Plant shedding its leaves; a. v. ♀ ♀, w. v. ♀ ♀, ♂ ♂ and sexual ♀ ♀ present; ova laid.

Euonymus E_9.—14. 9. 20. Infected with 15 w. v. ♀ ♀ from Beans B_4. This plant has a lot of young growth. 14. 10. 20. Many aphids present; ♂ ♂ and sexual ♀ ♀ present.

Euonymus E_{10}—11. 10. 20. Infected with 10 w. v. ♀ ♀ from Beans B_5. 14. 10. 20. Only two winged forms producing on the plant. 30. 10. 20. Offspring now adult, all sexual ♀ ♀, 16 in number.

Euonymus E_{11}.—(Kept in warm greenhouse.) 24. 11. 20. Infected with one w. v. ♀ from Beans B_7. 9. 12. 20. Offspring all oviparous ♀ ♀, 24 in number, some adult. 26. 12. 20. Ovip. ♀ ♀, large size; no ova produced.

Euonymus E_{12}.—25. 2. 21. Infected with one w. v. ♀ (sexupara) from Beans B_{18}. 12. 3. 21. Only oviparous ♀ ♀ produced, some nearly adult. 12. 4. 21. All the oviparous ♀ ♀ alive, have distended abdomen; no ova laid. Ova in the bodies, but females not fertilized.

II.—General Discussion.

A.—*Appearance of Winged Forms.*

It was almost universally held by the earlier investigators who studied the biology of Aphids that poor sap conditions obtaining in plants resulted in the production of winged forms. Later investigations indicated that temperature and humidity may also be important factors.

The results obtained by these earlier workers have been so often reviewed in the literature on Aphids that it seems unnecessary to review them again.

Starting therefore with Mordwilko (1907–1909), who in his extensive observations on the biology of Aphids gives a general idea of the views obtaining at that time, we see that food conditions, probably correlated with temperature, were accepted as the important factors.

Investigations during the next few years on the life cycle of Aphids from the cytological aspect lead one to the view that, although external factors may have some influence on the production of winged forms, there is in all probability some internal inherent mechanism at work which is the important factor.

Later results obtained from breeding experiments, notably by Klodnitzki (1912), Baker and Turner (1916), and Matheson (1919), in which winged forms were obtained in many of the parthenogenetic generations, would seem to support this view. The situation at present is, however, by no means clear, and external influences, especially of food and temperature, would appear to be very important factors in the results obtained by some recent workers, notably Ewing (1916) and Shinji (1918). In discussing this

question further, however, I hope to show with reference to the results of my experiments that those obtained by the latter authors are by no means conclusive.

Ewing, working with *Aphis avenae* Fab., considers temperature is the determining factor. The optimum temperature of 65° F. resulted in only apterous forms being produced during 20 parthenogenetic generations.

Klodnitzki obtained winged forms along with apterous forms in most generations when breeding the dark green and brown varieties of *Siphonophora* (Macrosiphum) *rosae* Koch, in normal and abnormally low temperatures. Similarly with *Aphis hederae* Kalt., over 35 agamic generations, winged forms appeared in low temperatures as in normal temperatures. There was a tendency for a. v. ♀ ♀ to produce winged forms.

Shinji investigated the influence of food conditions on the production of winged forms in Aphids. By growing cut stems of plants infected with aphids, in sand moistened with solutions of certain chemical substances, he obtained results which suggest that the percentage of winged forms produced was influenced. This was especially the case with solutions of Mg. sulphate.

The figures obtained are interesting, but a further investigation of the subject is desirable. It is necessary to know the history of the Aphids experimented with, and the number of the viviparous generation used. Comparisons between the effect on the offspring of w. v. ♀ ♀ and a. v. ♀ ♀ respectively should be observed. The varying individuality of the Aphids concerned, relative to an inherent tendency to wing development, should be known. Temperature and humidity factors must also be considered.

It will be seen in my experiments that winged forms appeared in most of the generations. Winged viviparous females produced as a rule only apterous viviparous females, although in one or two cases (see text, fig. 1) a few winged forms developed as well as apterous forms. Apterous viviparous females, offspring of w. v. ♀ ♀, usually produced a varying percentage of winged forms, although sometimes only a. v. ♀ ♀ were produced. This sequence was the same on different species of plants.

Winged forms have been obtained on young succulent shoots of *Euonymus europaeus* and apterous forms on "woody," non-succulent plants.

Food conditions, therefore, would appear not to be the deciding factor. The tendency appears to be for a. v. ♀ ♀ to produce a mixed progeny of w. v. ♀ ♀ and a. v. ♀ ♀, or in some cases only a. v. ♀ ♀. W. v. ♀ ♀, on the other hand, invariably produce a. v. ♀ ♀, with only occasionally winged forms in later generations. It is seen that when a plant, either the winter host (*Euonymus*), or an intermediate host (Beans), is infected, either with a. v. ♀ ♀ or w. v. ♀ ♀, and the Aphids allowed to reproduce freely on the

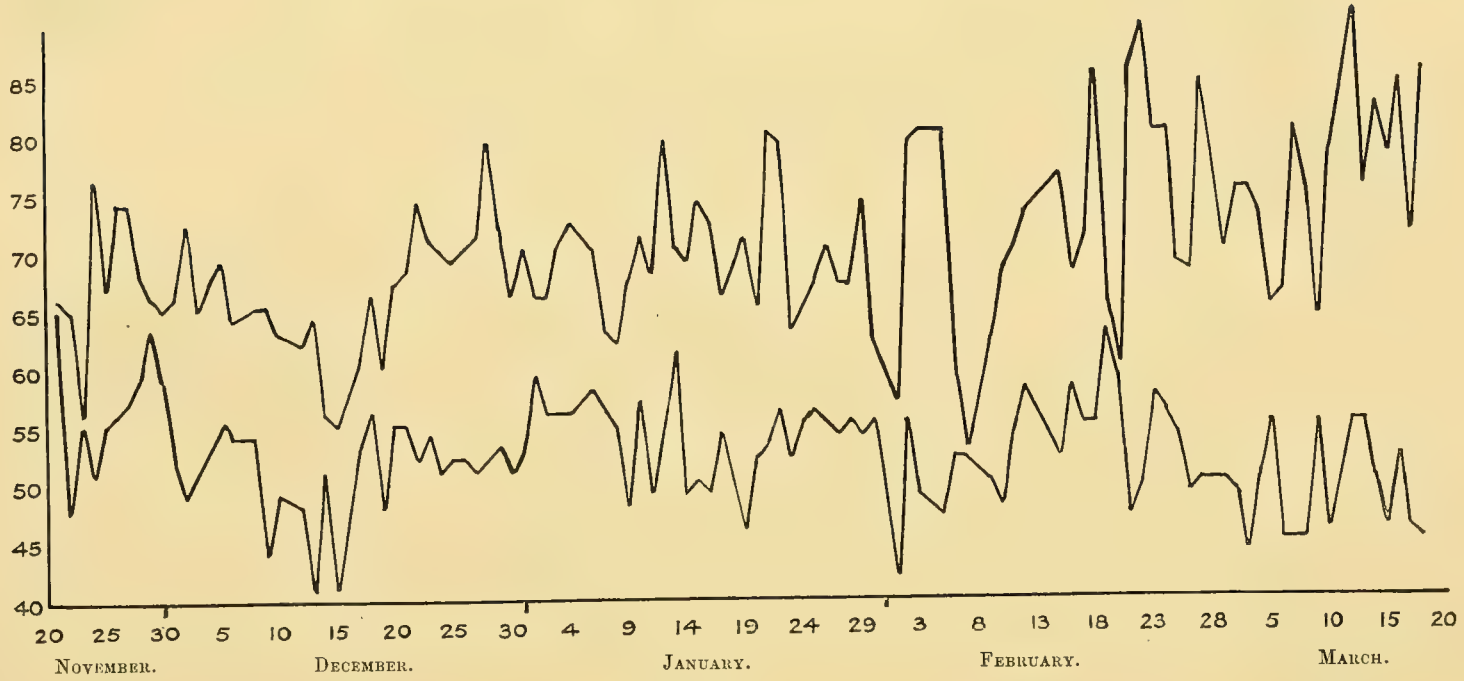

Fig. 2.

Temperature Chart of Green-house, November 21st, 1920, to March, 1921.

Upper line shows maximum daily temperature.
Lower line shows minimum daily temperature.

plant, winged forms always appear in due course. Although at the time that winged forms appear in great numbers the plant may be heavily infested, the appearance of the winged forms is not necessarily connected with the condition of the plant, but due to the innate tendency of the apterous females to produce winged forms as described above. It would seem that the overlooking of this fact has clouded the observations of earlier observers, who correlated the conditions of the plant with the appearance of winged forms.

The sequence of the development of winged forms on *Rumex*, *Euonymus* and Beans is well shown in figs. 1 and 3.

The percentage of winged forms which may develop in any generation as offspring of a. v. ♀ ♀, varies considerably.

The tendency for a higher percentage of winged forms to develop in some cases on Sugar Beet, Red Beet, and Poppies, and also on some varieties of Broad Beans, has been observed in my experiments.[1] It is not at all clear, however, that this can be considered as due to the nature of the cell sap of the different plants acting on the Aphid metabolism. Owing to the wide variation in the numbers of winged forms produced, it seems that factors other than food and temperature must be looked for.

In these experiments temperature and humidity varied, but the conditions were approximately the same for any series of experiments extending over the same period.

From my observations one is led to the view that the appearance of winged forms is determined by internal factors. It seems probable, however, that environmental conditions may exert an influence by restricting or favouring metabolism, and thus affecting the production of winged forms; but further experimental investigations in relation to temperature, humidity, and food factors and further cytological studies are necessary.

It seems to the author that the methods adopted for breeding Aphids may largely account for the conflicting results obtained by various workers. When one considers the number of offspring that an Aphid mother can produce, it is obvious that only an extremely small percentage of the Aphids in any generation can be isolated to carry on further generations.

From general observations on the progress of *Aphis rumicis* in colonies, there is a clearly indicated tendency for apterous viviparous females to eventually produce some winged forms. This inherent tendency may be more developed in some strains than in others, and a big element of chance occurs in the selection of Aphid mothers to carry on the generations.

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[1] *Vide* Davidson, J. (1921[a]).

Before one can investigate the influence of external factors on production of winged forms, it is necessary to estimate by extensive breeding experiments the extent and relations of this inherent tendency to wing-production

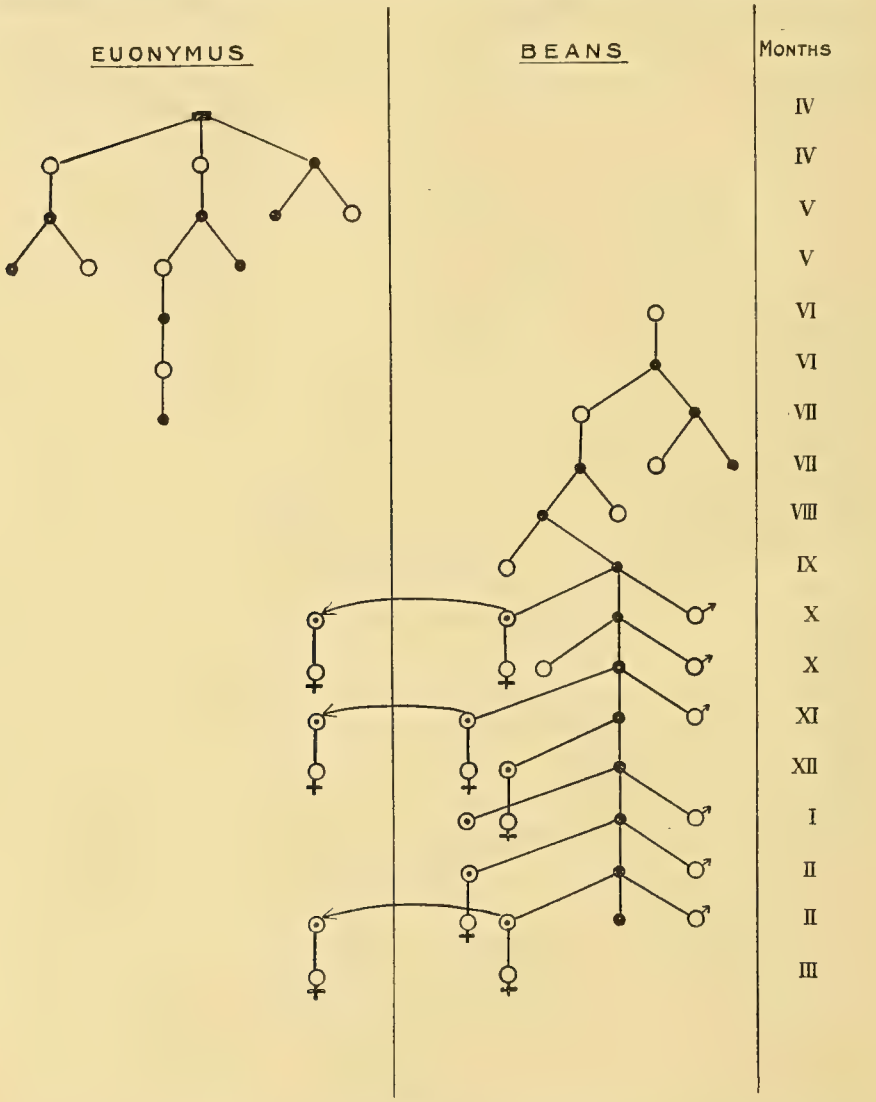


FIG. 3.

Illustrating, in successive generations of *A. rumicis*, the appearance of winged and apterous forms, also of sexual forms, on Broad Beans and Euonymus. The months are shown at the right-hand side. The series is being continued.

▬ Fundatrices. ● Apterous viviparous females. O Winged viviparous females. ⊙ Winged sexuparae. ♀ Sexual females. ♂ Males.

in different agamic females. It is generally considered that the winged condition is the more primitive, and that the apterous condition has arisen

later. In the loss of the wings, with the resulting change in body form, and in the loss of the sensoria on the antennae, is indicated a degeneration correlated with the more localized parasitic habits of the apterous form.

It seems to me therefore that external factors can only be considered as likely to exert an influence in restricting or favouring what is already present as an inherent tendency, and not in producing two complex dimorphic forms. Doubtless, external factors—food and climatic seasonal conditions—extending over long periods of time, have influenced the winged and apterous condition in the agamic generations.

(B).—*Appearance of Sexual Forms.*

The early conception of the alternation of sexual and parthenogenetic generations in the life cycle of Aphids was that external conditions—food and temperature—were the chief factors accounting for the appearance of the sexual forms and for bringing the parthenogenetic generations to an end. The experiments of several early workers, such as De Geer, Kyber, and others, whereby, with certain species of Aphids, parthenogenetic reproduction was continued for a great number of generations, under favourable food and temperature conditions, seemed to support this conception. Further, the view readily fitted in with general observations on Aphids in the field, namely, the widespread distribution of agamic females in the summer months and the occurrence of sexual forms in the autumn. Comparatively little experimental work on the *Aphididae* has been carried out, however; and the views held regarding Aphids are largely influenced by the results of the numerous researches on other animals, particularly the *Cladocera* and *Rotifera*, although in these cases sex appears to be largely determined by the chromosome complex.

The literature on this subject has been so frequently reviewed that it is not proposed to deal with it here.

With the development of the cytological aspect of the life cycle of the *Aphididae*, notably by Morgan, Stevens, Tanreuther, and von Baehr, it became clear that internal factors, closely associated with the chromosomes, must be considered of first importance. Whatever influence external factors may exert, they can hardly be considered as determining the sexual forms, although in the progress of adaptation and selection these factors have, doubtless, played an important part in favouring or restricting the parthenogenetic generations.

The more recent results obtained by breeding species of Aphids through several generations support the view that internal factors are the important ones concerned.

With individuals of some species, however, the parthenogenetic generations may be continued under favourable conditions for a long period, as has been shown in many cases. For example, Klodnitzki (1912) carried on agamic generations of *Siphonophora rosae var. glauca*, Buckton, for more than a year. Ewing (1916) carried on *Aphis avenae* for seventy-three parthenogenetic generations.

It would appear that in some species the sexual forms develop after a definite number of agamic generations have been passed through; but this is not the case in all species, as is seen in my experiments and in those of Davis (1914) with *Callipterus trifolii*, Monell.

A further consideration is that, while certain individuals of the later summer agamic generations close the life cycle by producing only sexual forms, other individuals may also produce agamic females which continue the agamic generations under favourable conditions for a very long period. Klodnitzki carried on three cultures of *Aphis hederae* Kalt. over a number of generations. In two lines sexual forms appeared in the thirty-first generation, but no sexual forms appeared in the other line, even after forty-two generations had been passed through. Davis (1915) observed a similar agamic series in *Macrosiphum pisi* Kalt.

The continuation of parthenogenetic reproduction throughout winter under favourable conditions of food and temperature has been obtained in my experiments with *Aphis rumicis*. With the advent of unfavourable winter conditions in the field, the agamic generations would die off, but under mild conditions, and given a suitable food-plant, they may survive the winter, and slowly carry on the parthenogenetic reproduction.

The finding of a colony of agamic females of *Aphis rumicis* by Davidson (1914) on January 30th, 1913, on *Euonymus japonicus*, which, when brought into the green-house, continued agamic reproduction throughout 1913, would seem to support the latter view. This is an important consideration from the economic standpoint.

It is possible, of course, that some late parthenogenetic generations, delayed in their development on the approach of winter conditions, would normally under favourable conditions lead to sexual forms.

It appears that in Aphids the development of viviparous parthenogenetic generations, between the ova and the sexual forms, is an expression of adaptation and selection to environmental conditions, extending over the favourable seasons of the year.

Certainly in nature the approach of winter conditions would normally be the factor limiting the extent to which the parthenogenetic phase could be extended.

In this respect it is interesting to refer to the life cycle of *Aphis saliceti*, a species in which the number of parthenogenetic generations is very limited, the sexual forms appearing in early summer. As shown by Klodnitzki, the ova hatch out in April and May. Some of the Fundatrices produce ♂ ♂ and sexual ♀ ♀; others produce w. v. ♀ ♀, which migrate to other willow trees, and produce ♂ ♂ and sexual ♀ ♀.

Passing now to Aphis rumicis, it is seen that the agamic generations are further extended over the favourable seasons of the year. Normally in nature, the approach of winter conditions will be the important factor in bringing these agamic generations to an end.

In view of the cytological investigations in Aphids, it seems evident that some factor or factors associated with an adaptation of Aphids to seasonal conditions cause a radical change in chromozome segregation, resulting in the development of sexual forms, and the production of ova at a period which ensures the continuation of the species.

It seems feasible to expect that with an extension of favourable seasonal conditions, such as would obtain in a warmer climate, there would be a corresponding extension (due to adaptation) of the agamic generations. This appears to be the case in *Aphis avenae* Fabr., and *Toxoptera graminum* Rond. in America.

It is clear from my experiments that certain of the apterous, parthenogenetic females may carry on the parthenogenetic strain throughout winter if given favourable food and temperature conditions. This cannot, however, be considered as wholly due to these two factors, because sexual forms and agamic forms appear together in each generation under the same environmental conditions. It is, I think, just a case of parthenogenetic ♀ ♀, which normally on the secondary host-plants would have died off on the approach of unfavourable weather conditions, being saved by keeping them in a suitable environment.

One cannot say at present how far these cases occur in the *Aphididae*. It is highly probable that in breeding experiments, considering the very small percentage of the offspring used in each generation, it is only by chance that individuals are selected which have the continuing parthenogenetic tendency.

It is seen in the series Broad Beans B, B_1, B_2, &c., as illustrated in fig. 3, that parthenogenetic individuals were carried on Beans from May onwards throughout the winter. In winter the plants were kept in a warm green-house, and fresh Bean plants were raised in succession for each generation. Towards October, sexual forms appeared, and in some lines of the cultures the cycle closed by the production of these forms. Some of the

infected plants were put into the warm green-house with the hope of carrying on the agamic generations, and the interesting result shown in fig. 3 has been obtained. After October had set in, there was a marked tendency to production of sexual forms, and the agamic forms in most cases died out.

However, in the case illustrated in fig. 3 a few agamic a. v. ♀ ♀ developed, and these were isolated, and their offspring carefully watched. In each succeeding generation large w. v. ♀ ♀ (winged sexuparae, ♀ producers) and winged ♂ ♂ were produced; and in every case one or two agamic a. v. ♀ ♀ also developed, which were isolated to carry on the next generation. It was not possible to follow out the exact numbers of each form produced, owing to the great number of pots and plants that would be required; but winged sexuparae were in the majority, with a comparatively small number of ♂ ♂. The agamic a. v. ♀ ♀, on the other hand, were usually only one, two, or three in each of the later generations.

The development period of these agamic individuals is somewhat longer than that of the summer generations, and the numbers of offspring produced considerably less. This may to some extent be due to low concentration of the cell sap of the plants, owing to conditions of winter sunshine and reduced assimilation.

It will be seen that agamic and sexual forms in the same generations were obtained on Euonymus.

The females produced by the winged sexuparae grew well on Broad Beans, and became larger than normal females; but in no case were ova laid, although on dissecting these females several large eggs were found inside them. These ♀ ♀ in the experiments were not fertilized, owing to the fact that the Aphids were removed from the plants as they became adult.

In one case ten oviparous ♀ ♀, born on a Bean plant on 1st January, 1921, had not produced ova by 16th February, and by that time only two ♀ ♀ were alive. When some of the females were dissected, they were found to contain several large eggs.

Sexual forms were produced when the Aphids were kept continuously on *Euonymus europaeus*, and also when they were kept continuously on Beans.

As referred to in a previous paper (1921), sexual forms have been recorded in the field on *Rumex*, Sugar Beet, and Haricot Beans. It is evident, therefore, that the food plant in itself does not determine the appearance of the sexual forms. It is very interesting that sexual forms appear on the primary or secondary host, showing that the distribution of

winged migrants over a great number of intermediate hosts is not an essential part of the life-history, but must be regarded as an adaptation to a search for more suitable food conditions.

One cannot consider, therefore, that *Aphis rumicis* is a true migratory species on which the influence of the intermediate host is an essential part of the life cycle. If suitable conditions are available, the life cycle can be passed through on either the primary or the secondary host.

These conclusions, however, are largely based on the behaviour of Aphids in captivity. It is obvious, from the nature of the primary host and the temporary life of the secondary hosts, that the migration from the one to the other at suitable seasons is decidedly of benefit to the Aphids under natural conditions. It does not preclude, however, two very important possibilities in the life cycle of *Aphis rumicis* in nature, namely, (*a*) the occurrence of agamic females, which may continue under mild winter conditions, and carry on agamic reproduction in the following season; (*b*) the occurrence of sexual forms and winter eggs on plants other than *Euonymus europacus*. These two possibilities may explain how, although one known winter host (*Euonymus europaeus*) of this species has a very localized distribution, the distribution of *Aphis rumicis* is a very wide one.

Unfavourable seasonal conditions over the period when sexuparae are being produced would result in a heavy mortality of the agamic forms, a reduction in the number of fertilized eggs laid, and a smaller outbreak of Aphids the following season.

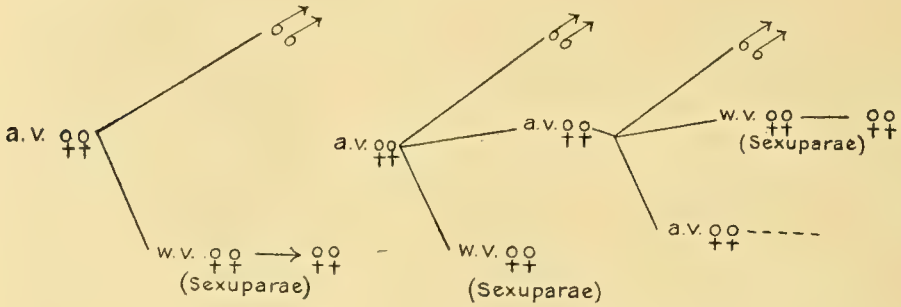
It has been shown that on the approach of autumn, the influence of some important factors results in the development of sexual forms irrespective of the number of the generation. There would appear to be at work some inherent tendency associated with adaptation to seasonal conditions. As autumn advances, an increased number of sexual forms appear.

♂ ♂ appeared on Euonymus E_2 on 10. 8. 20, and ♂ ♂ and sexual ♀ ♀ were present on Euonymus E_3 early in October. The sexual forms appeared also on Beans B_5 early in October. From September onwards an increasing number of sexual forms developed. In Beans B_{10} one agamic female continued parthenogenetic viviparous reproduction, giving rise to ♂ ♂, winged sexuparae and two a. v. ♀ ♀.

In my experiments the ♂ ♂ and oviparous ♀ ♀ were produced by different mothers, the winged sexuparae producing the oviparous females, and the a. v. ♀ ♀ (apterous sexuparae) producing the ♂ ♂.

The closing of the life cycle by the development of sexual forms

and the continuation of the agamic series may be shown in the following way :—



Klondnitzki found in *Aphis hederae* Kalt., that the sexuparae are apterous and the same mother produced both ♂ ♂ and ♀ ♀.

Baker and Turner (1916) found in *Aphis pomi* De Geer, that the same mother (sexuparae) could produce both sexes; and in one case a mother produced both sexes and agamic forms.

One can also consider in the case of *Aphis rumicis* that the same mother can give rise to both sexes, in that the winged sexuparae, which produce only sexual ♀ ♀, are presumably predestined in the original agamic mother to produce sexual ♀ ♀.

Similarly, both sexual and agamic forms are produced by the same mother.

From a colony of agamic apterous females—Beans B_5—all stages appeared in October, namely ♂ ♂, sexual ♀ ♀, a. v. ♀ ♀, and w. v. ♀ ♀.

In conclusion, it is seen that in my experiments sexual forms developed under favourable conditions of food and temperature. They may arise in different generations. They were produced under the low temperatures of October in the glass-house, and later under the warm temperature in the green-house. Further, agamic and sexual forms appeared together under the same conditions of food and temperature. The autumn seasonal factor would appear to be important in accounting for the large numbers of sexual forms produced at this period. It is difficult to believe that the influence of external factors is the important one, when one considers that under the same external conditions totally different forms are produced—namely, ♂ ♂, sexual ♀ ♀, and agamic females. Over long periods of time, external factors associated with seasonal conditions would be important, and it appears highly probable that the parthenogenetic and sexual phases are adaptations to seasonal conditions.

While the generative changes appear to be determined by an internal

mechanism associated with the chromosome complex, it seems feasible to expect that changes in the environment may, by influencing the metabolism of certain individuals, indirectly affect the natural sequence of chromosome segregation, and so affect sex-production.

This would allow of two conflicting views—internal mechanism and external factors—being brought into line, and would explain the result shown in figure 3.

External factors, therefore, may be regarded as exerting an influence by retarding, restricting, or favouring the appearance of sexual forms, and not as determining them.

III.—SUMMARY.

The early aphidologists considered that food and temperature conditions were the important factors influencing the apterous and winged forms in Aphids. This view appears to be upheld by the later experiments of Ewing and Shinji.

From cytological investigations on Aphids and recent breeding experiments, it appears highly probable that the sequence of winged and apterous forms is largely due to some internal, inherent tendency. W. v. ♀ ♀ tend to produce a. v. ♀ ♀, and a. v. ♀ ♀ to produce either a. v. ♀ ♀ or a mixed progeny, including a very variable percentage of winged forms. The apterous condition is to be regarded as an adaptation to seasonal food and temperature conditions. The great variability in the numbers of winged forms produced by apterous individuals is an important point to consider.

Similarly, food and temperature conditions were considered the important factors affecting the development of sexual forms. Later cytological investigations show that the appearance of the sexual forms is associated with changes in the chromosome complex. The agamic generations appear to be interpolated between the winter egg and the sexual generation as an adaptation to seasonal conditions. The approach of winter conditions would normally be the factor affecting the bringing to an end of the parthenogenetic phase and the appearance of the sexual forms.

In some cases the production of sexual forms may be superseded by continued parthenogenetic reproduction, certain agamic forms either reproducing slowly throughout a mild winter, or lying dormant and continuing reproduction the following season. In isolated cases, certain agamic individuals may be affected physiologically by some factor or factors acting on their metabolism, so that they do not respond to the inherent stimulus to develop into sexual forms. These individuals normally, in winter, would die, but under favourable conditions may continue agamic reproduction.

From the observations of other authors, however, it is evident that generalizations on the biology of the *Aphididae*, as a whole, cannot be drawn from the study of one species. Many special characteristics are exhibited by some species, owing to the complexity of the life cycle. Further investigations on the cytology of Aphids made in conjunction with breeding experiments are necessary for a clearer understanding of the biology of the *Aphididae*.

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XXVI.

THE OCCURRENCE OF DEWALQUEA IN THE COAL-BORE AT WASHING BAY.

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AND
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[Plates XI, XII.]

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In 1918 a boring to test the position of the concealed coalfield was begun by the Ministry of Munitions at Washing Bay, at the south-west corner of Lough Neagh. Owing to the unexpectedly enormous thickness of the beds of clay and basalt (1,500 feet instead of 250 feet estimated), the operations have been abandoned. The core has been placed in charge of the Geological Survey. Early in 1919 Mr. W. B. Wright, F.G.S., brought one of us pieces of the core containing plant remains for identification. For the past two years all available time has been devoted to the investigation of these remains, and many interesting results have been obtained.

We are indebted to Professor G. A. J. Cole, F.R.S., Director of the Geological Survey, for permission to examine the core, and to Mr. Wright for the following observations on the geological features of the district:—

"The boring put down by the Ministry of Munitions in the years 1918 and 1919 in search of the concealed coalfield supposed to exist beneath the Lough Neagh basin has yielded the first reliable evidence regarding the geological age of the Lough Neagh beds. The site selected was at Washing Bay, about four miles east of Coalisland, Co. Tyrone. The bore entered the Lough Neagh beds, beneath the glacial drift, at a depth of 48 feet, and reached the base of these beds at 1,196 feet 2 inches. The basal beds of the Lough Neagh series rested on about 70 feet of lithomarge produced by the decomposition of the Upper Basaltic lavas of Co. Antrim, which are well represented below. The series is, therefore, distintly post-basaltic in age, and is to be

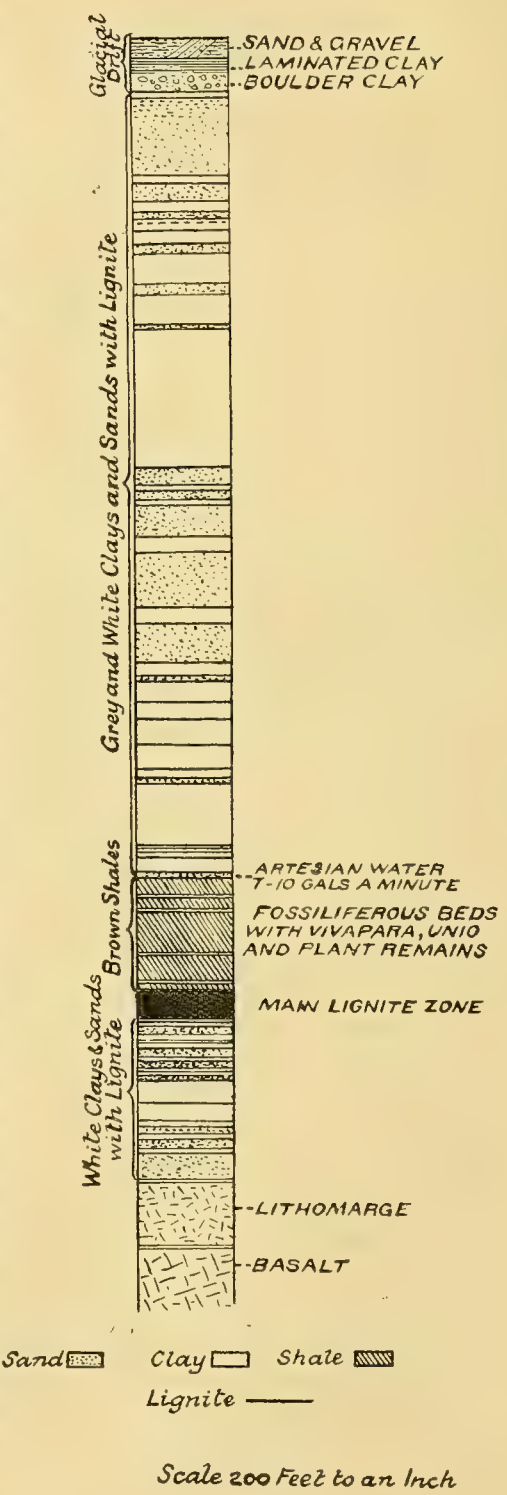
[1] Miss Gilmore's help was rendered possible by a grant from the Department of Industrial and Scientific Research.

referred to a later date than the plant-bearing beds of inter-basaltic age, which occur at Ballypallady. The Basaltic series of Co. Antrim rests as a whole on the chalk, which is of Upper Cretaceous age, and contains the zone of *Belemnitella mucronata.*

"The facts established by the boring, combined with certain relations observable at the surface and hitherto imperfectly understood, indicate with a fair amount of certainty that the Tertiary folding and faulting of the district affect equally the Lough Neagh beds and the lavas on which they rest. The earth movements which resulted in this folding and faulting are, for reasons which cannot be entered into here, generally considered to be of Miocene age. The Lough Neagh series is, therefore, presumably pre-Miocene. It is certainly not later than early Miocene.

"The stratigraphy of the Lough Neagh beds is exhibited in the accompanying diagram. The main horizons of identifiable plant remains occurred in the brown shales or clays between the depths of 881 feet and 1,008 feet 7 inches, lying mainly in the upper portions of these shales. The plant remains in the white clays above and below these beds were for the most part unidentifiable, being highly carbonized.

"From the geological relations alone it is impossible to draw any more exact conclusion regarding the



age of these beds than is embraced in the general statement that they come in somewhere between late Cretaceous and early Miocene times. As, however, the lake basin in which they were laid down was probably produced by some early forerunner of the Miocene earth-movement, there is a presumption in favour of the later portions of this long epoch.

" It is obvious that any palaeontological evidence that is obtainable becomes of very great importance in determining with more precision the horizon of the clays. Such a determination, moreover, would also assign an upper limit to the age of the great series of basaltic eruptions in north-eastern Ireland."

One of the most interesting fossils found in the coal-bore is the genus *Dewalquea*.

Our first recognized specimen occurs in the core at a depth of 903 feet, and reveals itself as a five-lobed leaf (Pl. XI, fig. 1) in all essential features, in agreement with the *Dewalqueas* of the European Continent and America. The whole leaf is 9 cm. long by 9 cm. broad; the petiole being only partially preserved, is not included in the measurement. The petiole divides at its distal end into three branches, the two outer ones branching again. Each of the five branches carries a lanceolate, acuminate, toothed, coriaceous leaflet. The leaf is clearly compound, quinately palmate or pedate, not a simple palmatisect or pedatisect leaf. The medium leaflet is 8 × 1·5 cm., the inner lateral ones 7 × 1·5 cm., while the outer ones are much smaller, being 0·8 cm. wide, and probably only 4 cm. long. Neither leaflet of the outer pair is completely preserved in the specimen. The median petiolule is 3 mm. long, the lateral ones are 7 mm. long, and their branches very short. The base of the median leaflet is symmetrical and attenuated; the bases of the others are asymmetrical. The base of each inner lateral leaflet has the lamina prolonged downwards on its inner side beyond the outer lamina, the converse being the case with the outer pair—clearly an adaptation of shape to space requirements. The edge of each leaflet is entire in its basal part, but serrate in the upper two-thirds of its length.

We have been able to restore the epidermis on both sides of the leaf. The upper and under epidermides (Pl. XII, figs. 5–8) consist of cells with more or less pronounced sinuous lateral walls. The lower epidermis shows numerous sinuous cuticular striae on the outer face of the cells. Similar striae are described by Nestler (1) in *Helleborus*, in which they are confined to the upper epidermis. The upper epidermis of our fossil shows minute cuticular tubercles like those on the under epidermis in *Hellebore*. Stomata are confined to the lower epidermis. They are 35–40μ in diameter, sub-circular in outline, without subsidiary cells. Peltate scales, circular

in outline, 60–76μ wide, and consisting of a shield of 6–8 cells on a short stalk, are frequent, and are observable even with the lens on the counterpart impression through becoming detached from the leaf-surface (Pl. XII, figs. 1–2). These peltate scales and the cuticular striae have not been found previously in *Dewalquea*, and must be taken into account in considering its systematic position.

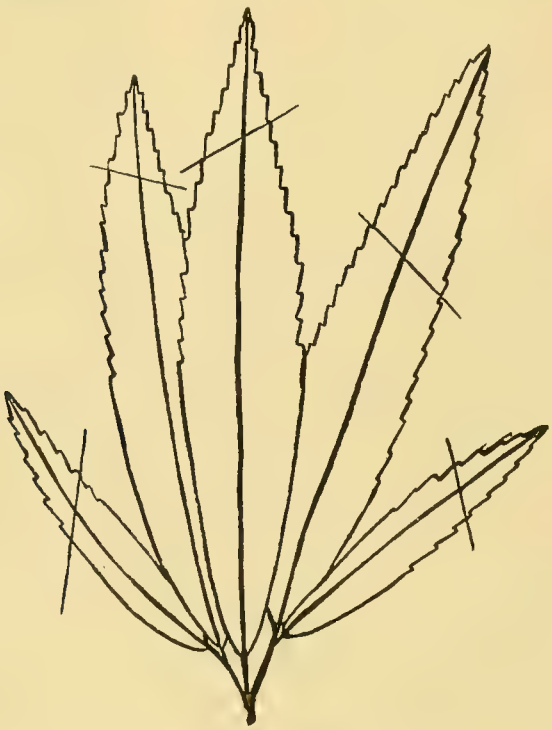


Fig. 1.—*Dewalquea hibernica* $\frac{3}{2}$ Restoration.

Fig. 2.—*D. fraxinifolia* $\frac{1}{1}$ Restoration.

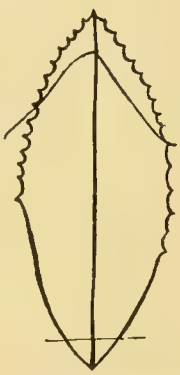


Fig. 3.—*D. denticulata* $\frac{1}{1}$ Restoration.

We propose to call the specimen just described *D. hibernica*. There are

many other examples of the genus in the core between 897–913 feet, as well as at 787 feet. One leaf shows three leaflets, and may be named *D. fraxinifolia* (Pl. XI, fig. 4). Another apparently simple leaf we propose to call *D. denticulata* (Pl. XI, fig. 11). Most of the other specimens—some twenty in all—are fragments of leaves only. They all show the *Dewalquea* type of tissue, and indicate that it was common in the locality.

Affinities of Dewalquea.

The discovery of *Dewalquea* was made by Debey in the Senonian (Upper Cretaceous) of Westphalia. He appears to have sent specimens and drawings to Saporta and Marion (2), then at work on the Belgian Tertiary flora, and also to Schimper (3). Debey's MS. name of *Araliophyllum*, accepted by Schimper, was not, however, adopted by Saporta and Marion, who replaced it by *Dewalquea* (after the Belgian geologist), three specimens being described—*D. haldemiana* S. and M. and *D. aquisgranensis* S. and M. from Westphalia, and *D. gelindenensis* S. and M. from the basal Eocene of Gelinden. Since 1874 other species have been described, of which Berry (4) gives a useful critical revision. They are all, with one exception, from the Upper Cretaceous, and are from America. One of the species, *D. Smithi*, is founded by Berry on material from the Tuscaloosa (Upper Cretaceous) beds of Alabama. *D. Smithi* is very similar to, but distinct from, *D. insignis* Hosius and von Marck from Haldem (Westphalia) (5). It differs from all previously recorded American species in being quinate, not ternate. It is similar to *D. coriacea* and *D. pentaphylla*, found by Velenovsky (6) in the Cenomanian of Bohemia. Knowlton (17), in 1917, described a second quinate specimen *D. pulchella*, which he considered closely allied to, if not identical with, *D. insignis* H. and von M. *Dewalquea* is an extinct type of leaf derivable from or of the same type as *Polytaenia quinquesecta* of the Turonian. It occurs in the Upper Cretaceous from Alabama to Greenland, in Westphalia and Bohemia, the Lower Eocene of Gelinden, in Belgium, and in the Oligocene of Italy. The recorded distribution in time and space adds considerably to the interest of the discovery of a *Dewalquea* in the coal-bore at Washing Bay. If the deposit be correctly referred to the Upper Oligocene, the Irish specimen may represent the last trace of the genus in time. The five-lobed form (Pl. XI, fig. 1) is closely allied to *D. Smithi* Berry. The chief obvious difference is the smaller outer leaflets of the Irish specimen. Berry shows a craspedodrome venation in his restoration, but in his description says it may be camptodrome. Our five-lobed specimen is camptodrome, and is more comparable to the small specimen of *D. insignis* H. and von M. (*op. cit.*). It is unfortunate that *Dewalquea* is known by its foliage only (in many cases fragmentary), and

that identifications have been hitherto, of necessity, based on the macroscopic characters—on the shape, mode of segmentation, and type of venation; with the exception of an observation by Saporta and Marion, nothing hitherto has been revealed of the character of the epidermis. We propose to review the affinities suggested by previous observers in the light of our observations.

Helleborus Affinities.

Saporta and Marion base their rejection of Debey's reference of *Dewalquea* to *Araliophyllum*, and their own reference of it to the Helleboreae, mainly on the peculiar mode of segmentation of the leaf indicated by the term pedalo-digitate. The *Dewalquea* likeness is best indicated in *Helleborus foetidus*, as monographed by V. Schiffner (7). Its leaf is always distinctly pedately divided, and consists of 7–10 small, lanceolate, finely sharp-toothed leaflets. We have failed to note the agreement of the venation of *Dewalquea* with that of *Hellebore*, observed by Saporta and Marion, who were not so fortunate as ourselves in the state of preservation of their specimens, judging from the remark of Hosius and von Marck that the Westphalian material showed poorly preserved secondary veins. We give actual photographic illustrations of the magnified venation of *D. fraxinifolia* (Pl. XII, fig. 3). The secondary veins in *Hellebore* arise at a very acute angle from the midrib, send off branches right and left, and end like their outer branches in the teeth of the leaflet. Each secondary vein is craspedodrome. In *Dewalquea* the secondary veins come off at an angle of 60°–70°, and on nearing the margin bifurcate to join by their forks with adjoining secondaries, which then form a marginal network. They are thus camptodrome. A detailed comparison of the venation does not support the Hellebore affinities of *Dewalquea*. Saporta and Marion describe the epidermis of *Dewalquea* as formed of rounded polygonal cells, with probably sinuous walls like those in *Helleborus*, and, we may add, in many other genera.

Nestler gives a fully illustrated account of the structure of *Helleborus*. Stomata, 45 × 33μ, occur scattered on the under epidermis only. The lateral walls of the lower epidermis cells are sinuous. Unicellular hairs occur, as in Ranunculaceae generally. The upper epidermis shows marked cuticular striation. Peltate hairs are unknown in *Hellebore* or any other Ranunculaceus plant. The geographical distribution is also of interest. The Lower Danube is the "Eldorado" of *Helleborus*, which is exclusively Old World, while *Dewalquea* is represented by many species in the New World, as well as by several in Europe. It would, however, be dangerous to support conclusions of affinities on present-day distribution, there being many cases in which fossil fruits prove the former wider occurrence of a genus or family. The

Ranunculaceae, consisting almost entirely of herbaceous plants, would not lend themselves to fossilization, and their past history is almost a blank in the rocks, though, as members of the *Polycarpieae*, they must have been one of the earliest families of the Dicotyledons to appear. Hellebore, with its coriaceous leaves in some species, would be the one most likely to be found in the fossil state. It would be distinctly satisfying if *Dewalquea* could be accepted as the ancestral form of the family. Its peltate scales, combined with other features, militate, however, against this view.

The Araceae have been suggested as a possible line of affinity with *Dewalquea*. This is admittedly one of the most primitive families of the Monocotyledons, and in, *e.g.* Anthurium, there are several species with pedalo-digitate leaves. Their venation differs, especially in the possession of a marginal vein not found in *Dewalquea*. Their epidermis and stomata also differ. Peltate scales are said to occur, but they are simply saucer-like depressions, in which the secretion of the glandular epidermal cells collects.

A third line of affinity is that indicated by Debey's name of *Araliophyllum*. The *Araliaceae* were rejected by Saporta and Marion on the expert advice of Decaisne that leaves showing such segmentation were not then (as they are now) known in the group. Schimper, as already mentioned, accepted the generic name, and described the fossils as Araliaceous. Peltate hairs occur in *Hedera helix* and in *Oreopanax*, but they are stellate, and do not suggest the disc-like scale-hairs of *Dewalquea*.

P. Principi (8), in his recently published work on the fossil Dicotyledons of the Italian Oligocene, records the Belgian species, *Dewalquea gelindenensis*, and a new species, *D. grandifolia*. He follows Schimper and Zeiller (9) in referring the genus to the *Araliaceae*. *D. grandifolia* shows 5–7 leaflets, each on its own stalk, *i.e.* a compound leaf with 5–7 pinnately arranged terminal leaflets.

The Washing Bay flora is an early one from the Dicotyledonous point of view, and one would hardly expect to find highly specialized families such as the Oleaceae to be well represented in it. Thus in *Fraxinus excelsior* the corolla has passed through the stage of gamopetaly to suppression. *Fraxinus* first appeared in the Arctic regions, and gradually spread southwards in the Old and New Worlds. Heer (10) records *F. praecox* from the Upper Cretaceous beds of Patoot in Greenland; and Lesquereux (11) describes *F. cocenica* from the Eocene of Golden, Colorado; while Ettingshausen and Gardner (12) list *F. jovis* and *F. prae-savinensis* from Alum Bay. The seventeen European species recorded are nearly all referred to the Miocene. One of our specimens (Pl. XI, fig. 6), found at 909 feet, had every appearance of being the distal end of an Ash leaf, such as *Fraxinus pennsylvatica* var. *lanceolata*.

This identification was supported by comparison of the restored epidermis with that of Ash. The subsequent discovery of the quinately divided leaf of *Dewalquea* at 903 feet, with typical epidermal structure, seemed to indicate the necessity of a revision of the first view. In both *Dewalquea* and *Fraxinus* the venation, epidermis, stomata, and peltate scales (glands) all agree sufficiently to allow approximation; and we are of opinion that *Dewalquea* is more naturally associated with the *Oleaceae* than with the *Ranunculaceae.* There is, however, another line of affinity which appeals more to us.

Pl. XI, fig. 9, shows a well-preserved fossil leaf or leaflet, 2 × 4 cm., approximately, coriaceous, broadly oval-lanceolate, margin entire below, but sinuous-dentate in its upper two-thirds, midrib pronounced, thinning out apically; secondary veins fairly numerous but delicate, sub-opposite; angle of divergence, 70°–75°; adjoining secondary veins united towards the leaf edge by loops or their own forkings, and forming a marginal network, from which veins pass into the teeth; the whole system camptodrome. There are no pronounced cross-anastomoses, but there is a fairly well-developed vascular network forming polygonal areas between the secondaries. Shortened secondary veins occur. Externally this leaf shows great resemblance to *Ilex celastrina* Sap. (13), from the Upper Oligocene of Saint Jean de Garquier and Armissan in the south-east of France. As the name suggests, Saporta saw affinity in his specimen to *Celastrus* also, and admits, in naming it, that it is fairly remote in its characters from the *Ilex* of to-day.

If we were confined to a comparison of the external characters only, we should feel compelled to name our specimen *Ilex celastrina.* Restoration of the leaf tissue, however, alters our attitude. Markedly wavy walls are not found in *Ilex* epidermis, nor are peltate scales found in any of the *Aquifoliaceae,* according to Solereder (14). Of the many other possible connexions, the one combining most of the external and anatomical features is the genus *Carya, e.g.,* the modern *Carya laciniosa,* in which, however, tufts of hair, not known in our fossil, occur. Our specimen shows, however, such general agreement with *Dewalquea* in its external features and minute structure that we feel compelled to refer it to this genus and not to *Carya,* and to name it *Dewalquea denticulata.* We are of opinion that the leaf fragment named by Heer, *Pterocarya denticulata* ? (15) (*Juglans denticulata* O. Weber) from Bovey Tracey (*op. cit.,* Pl. LXX, fig. 5) is near to, if not identical with, *D. denticulata*; and that the *Carya bilinica* Ettings (16) is also probably nearly allied to it, though differing in form. A re-examination of the collections of fossils in our museums, after restoration by maceration, would reveal many hidden affinities.

Dewalquea shows certain Juglandaceous characteristics not to be overlooked in seeking to ascertain its systematic position. Principi's *D. grandifolia* shows a pinnate leaf of 5–7 leaflets derivable from the types illustrated in the earlier works quoted. The transition from the pedalo-digitate to the impari-pinnate leaf is not difficult to follow. In the seedling of *Pterocarya fraxinifolia* Spach., the two cotyledons are deeply four or five-lobed, and may be described as pedalo-digitate. Such a form of seed-leaf makes it unnecessary to look to the *Hellebore* for an explanation of *Dewalquea's* leaf. Examination of the adult pinnate leaf of *Pterocarya* (and of other genera of the Juglandaceae) shows the presence of peltate scales or glands which bear a striking resemblance to those of *Dewalquea*. In *Engelhardtia* the likeness is such that (Pl. XII, fig. 12) one might easily be mistaken for the other.

The epidermal cells show similar sinuous lateral walls, cuticular surface striae, and similar stomata. There is the same difference in the edge of the leaf as in *Dewalquea*. The edge may be entire or serrate in both genera—in different species in Juglans—but, according to Berry, possibly in the same species (or even plant) in *Dewalquea*. This difference of the leaf-margin is accompanied by a slight difference of venation, which is, generally speaking, camptodrome in Juglans. In this genus the cross-anastomoses connecting the secondary veins run straight and parallel to one another in most cases; but in *Engelhardtia* they are jointed and branched and irregular, as in *Dewalquea*. The secondary veins bifurcate and join together, giving a marginal network much as in *Dewalquea*. The *Juglandaceae* are a primitive group allied to the Amentaceae and Myricaceae. Though *Juglans* is now confined, in Europe, to the south-east corner, it was widely distributed throughout the continent in Tertiary times, having travelled southwards from the Arctic regions. Until fruits are found the question must remain open; but one may provisionally regard *Dewalquea* as an ancestral Walnut.

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EXPLANATION OF PLATES.

PLATE XI.

Figs.

1, 2, 3. *D. hibernica,* sp. n.

1. More or less complete leaf, showing five leaflets.

4–11. *D. fraxinifolia,* sp. n., showing the three leaflets of the leaf in varying degrees of preservation.

8, 9. The two impressions of the same leaflet. (× 2).

12–14. *D. denticulata,* sp. n.

13, 14. Natural size. Fig. 12 (× $\frac{3}{2}$).

PLATE XII.

1, 2. *D. hibernica,* showing the peltate scales. (× 2).

3. *D. fraxinifolia,* venation in detail. (× $7\frac{1}{2}$.)

4. *D. denticulata,* venation. (× 3.)

5, 6. Upper epidermis of leaf of *Dewalquea*, sinuous lateral walls.

7–10. Under epidemis of same, showing stomata and bases of peltate scales. (7–8 (× 80), 9–10 (× 360.))

11. Peltate scale of *Dewalquea.* (× 300.)

12. Peltate scale of *Engelhardtia spicata.* (× 300.)

XXVII.

A SIMPLE FORM OF APPARATUS FOR OBSERVING THE RATE OF REACTION BETWEEN GASES AND LIQUIDS, AND ITS USE IN DETERMINING THE RATE OF SOLUTION OF OXYGEN BY WATER UNDER DIFFERENT CONDITIONS OF MIXING.

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I.—Introduction.

The apparatus described in this paper was primarily devised as an alternative method of carrying out the "Five Days' Dissolved Oxygen Absorption Test," and is based on a principle previously utilized by Professor Adeney for the same purpose.[1]

In the course of the work, however, it became apparent that the principle was capable of wider application, and the apparatus was finally designed with a view to its possible use for the study of gas-liquid systems in general.

The effect of different rates of stirring on the rate of solution of oxygen in water has been determined by means of the apparatus, and the results of the experiments are given in this communication, as they have a direct bearing on some previously published work.[2]

II.—The Principle on which the Apparatus is Based.

The principle utilized in the apparatus depends on the changes in pressure which occur when a liquid is placed in contact with a closed volume of a gas which it is capable of absorbing, and the action of the apparatus will be understood by reference to fig. 1.

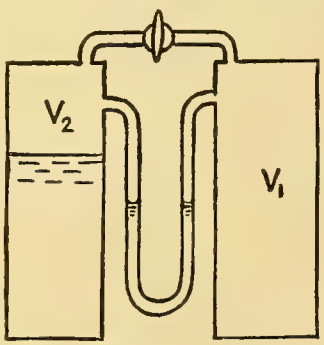

Fig. 1.

In the system shown in the diagram there is a volume of gas V_2 connected through a manometer with a volume of gas V_1, there being sufficient liquid in V_1 to ensure saturation of the gas with vapour, and the liquid under test

[1] Fifth Report, Royal Commission on Sewage Disposal. Appendix vi, p. 438.
[2] Adeney and Becker; Scientific Proc., R.D.S., 1919, xv, p. 609.

is in contact with the gas in V_2. When the tap is closed, any absorption of gas by the liquid from V_2 results in a decrease in pressure, which is indicated on the manometer, and from the manometer reading the volume of gas absorbed can be calculated. With such an arrangement it is possible to vary the sensitivity of the manometer considerably. The smaller the volume V_2 becomes in comparison with V_1, the greater the movement of the manometer (within limits) for a given absorption of gas by the liquid. Further, when the tap connecting V_2 and V_1 is opened, the manometer returns to zero, and the difference in pressure previously existing in V_2 is distributed between the combined volume, thus making it a much smaller fraction of the whole. With such an arrangement it becomes possible to reset the manometer to zero several times during the course of an experiment, without allowing the pressure in V_2 to fall to such a value as would seriously affect the solubility of the gas. The tap also affords an easy method of replenishing the supply of one of the constituent gases of a mixture contained in V_2. Thus, if V_2 contains atmospheric air in contact with a liquid absorbing oxygen, and V_1 contains pure oxygen, then, after a given absorption, the opening of tap resets the manometer, and also replaces the oxygen absorbed to an extent which will depend on the ratio $\frac{V_2}{V_1}$.

The conditions at the start of an experiment are such that the pressures in V_1 and V_2 are equal to each other and to the atmospheric pressure P mm.

Now, suppose an absorption of Q c.c. takes place in V_2, and that the resulting manometer reading is p mm., then $(V_2 - Q)$ c.c. at P are occupying $(V_2 - v_1)$ at P_x, where v_1 = the volume of liquid which has risen above the zero point in the manometer, and V_1 c.c. at P are occupying $(V_1 + v_1)$ c.c. at P_y.

Now, since $$P_y = P_x + p,$$

$$\therefore \quad \frac{PV_1}{V_1 + v_1} = \frac{P(V_2 - Q)}{V_2 - v_1} + p,$$

which gives $$Q = v_1\frac{(V_2 + V_1)}{V_1 + v_1} + \frac{p}{P}(V_2 - v_1).$$

If the two vessels are now connected by opening the tap, P_y becomes equal to P_x, and $p = 0$.

There is then $V_1 + (V_2 - Q)$ c.c. at P occupying a volume $V_1 + V_2$ at P_z.

Hence $$P_z = \frac{P(V_1 + V_2 - Q)}{V_1 + V_2}$$

$$= P\left(1 - \frac{Q}{V_1 + V_2}\right).$$

Hence the pressure in the air spaces after resetting the manometer will be less than that existing at the start by a quantity dependent on the ratio of the volume of gas absorbed to the combined volume of the two air spaces. By making the latter large this quantity can be made very small at will.

III.—Description of Apparatus.

The apparatus which was devised on this principle is shown diagrammatically in fig. 2.

It consists of two cylindrical glass vessels about 30 mm. in diameter, which are connected to two branches of a three-way tap. The lower vessel is of such a size as to contain a suitable volume (say 100 c.c.) of the liquid to be tested, and still leave room for an air space of about 50 c.c.; the upper vessel has also a capacity of about 50 c.c. The three-way tap allows of the two air spaces being connected through the manometer, or directly, according to its position. Hence, when an absorption has taken place, the manometer can be reset to zero by suitably turning the tap.

The whole apparatus, including the manometer, is enclosed in a cylindrical water-jacket, through which water is circulated from a thermostat. The handle of the three-way tap projects through a hole blown in this water-jacket, the joint being kept water-tight by means of a rubber diaphragm. The water-jacket is closed at each end by flanges, which may be made of brass, tin, or ebonite, according to the purpose for which the apparatus is to be used.

The stirrer passes through a long sleeve in the lower flange, and is provided with two conical surfaces, one of which can be

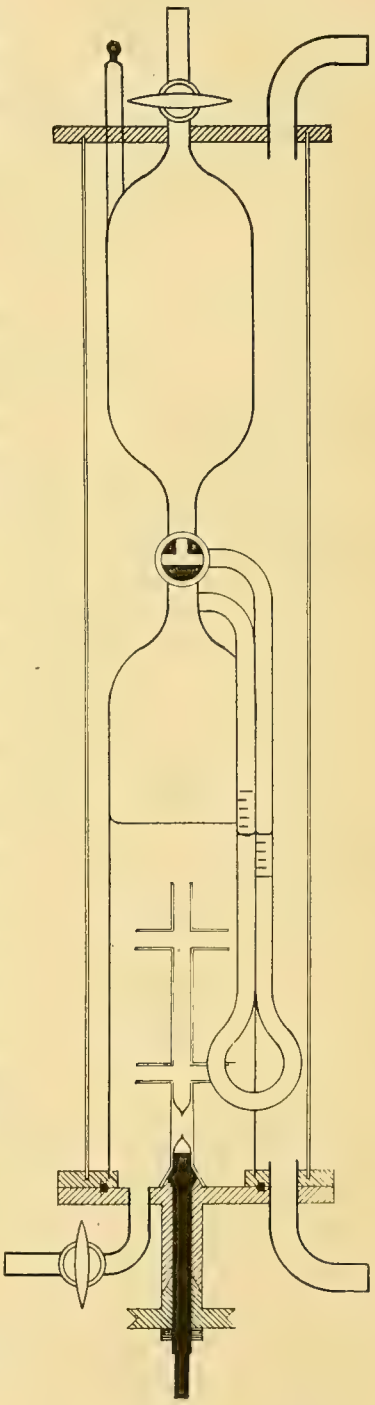

Fig. 2.

adjusted by means of a screw, so that the whole is water-tight. In addition, the glass part of the stirrer is expanded into a cone at the lower end, which is ground to fit a corresponding cone on the bearing, so that the metallic parts of the stirrer do not come into contact with the liquid at any point.

The glass part of the stirrer is so designed that, when rotated at a high speed, it causes a stream of fine bubbles of the gas to circulate through the liquid, thus ensuring equilibrium between the liquid and the gas.

The manometer is provided with a scale of millimeters etched on the glass.

IV.—Calibration of the Apparatus.

In order to check the formula derived for the calculation of the volume of gas absorbed, use was made of ferrous hydrate as an absorbent for oxygen. The following experiments were made:—

The apparatus was filled with 110 c.c. of distilled water which had been previously saturated with air at 20° C. by bubbling air through it for some hours, and the water circulation from the thermostat through the water-jacket started. When everything was in equilibrium, about 25 c.c. of the water was withdrawn, and in place of it was added exactly 10 c.c. of a solution of ferrous sulphate containing 8·2 grams per litre, followed by 10 c.c. of a 10 per cent. solution of sodium carbonate, the whole being carefully washed into the apparatus. The barometer was then read, and the taps of the apparatus having been suitably adjusted, the stirrer was started, and the manometer watched until the reading became constant. The maximum reading was then used to calculate the volume of oxygen absorbed by the ferrous hydrate.

Experiment A.—Temperature, 20·0° C.; barometer, 768·1 mm.

Maximum reading of manometer,	. 114·0	divisions.
Second reading after resetting to zero,	. 5·5	„
114 divisions at 768·1 mm. correspond to	1·525	c.c.
5·5 „ „ „	·073	„
	Total, 1·598	

Total volume absorbed, calculated for N.T.P. = 1·504 c.c.

Experiment B.—Temperature, 20·0° C.; barometer, 769.9 mm.

Maximum reading of manometer, 118 divisions.

118 divisions at 769·9 mm. correspond to 1·610 c.c., which at N.T.P. reduces to 1·520 c.c.

The mean of the two experiments gives 1·512 c.c. absorbed.

Since the partial pressure of the oxygen in the air in the vessel was

reduced from $\frac{10{\cdot}5}{50}$ to $\frac{9{\cdot}0}{50}$, a correction for this must be applied. The pressure in the vessel before the experiments was 768·1 mm., and at the end was 758·0 mm.

Taking the composition of atmospheric air to be approximately: nitrogen, 79 per cent., oxygen, 21 per cent., and the coefficient of absorption of oxygen as 0·0310 at 20° C., we can calculate the amounts of oxygen in solution at the beginning and at the end of the experiments.

The pressure of aqueous vapour at 20·0° C. is 17·5 mm.

The volume of oxygen in solution at the start is—

$$V_0 = {\cdot}0310 \times 110 \times \frac{10{\cdot}5}{50} \times \frac{750{\cdot}6}{760} = {\cdot}706 \text{ c.c.}$$

The volume in solution at the end is—

$$V_1 = {\cdot}0310 \times 110 \times \frac{9}{50} \times \frac{740{\cdot}5}{760} = {\cdot}598 \text{ c.c.}$$

Hence the difference due to change in the saturation value is ·108 c.c., and this, when added to the volume indicated by the manometer reading, gives a total of 1·62 c.c. as the actual absorption.

The 10 c.c. of ferrous sulphate used should have absorbed 1·64 c.c. oxygen according to its titre by potassium permanganate, hence the two values agree within $1\frac{1}{4}$ per cent.

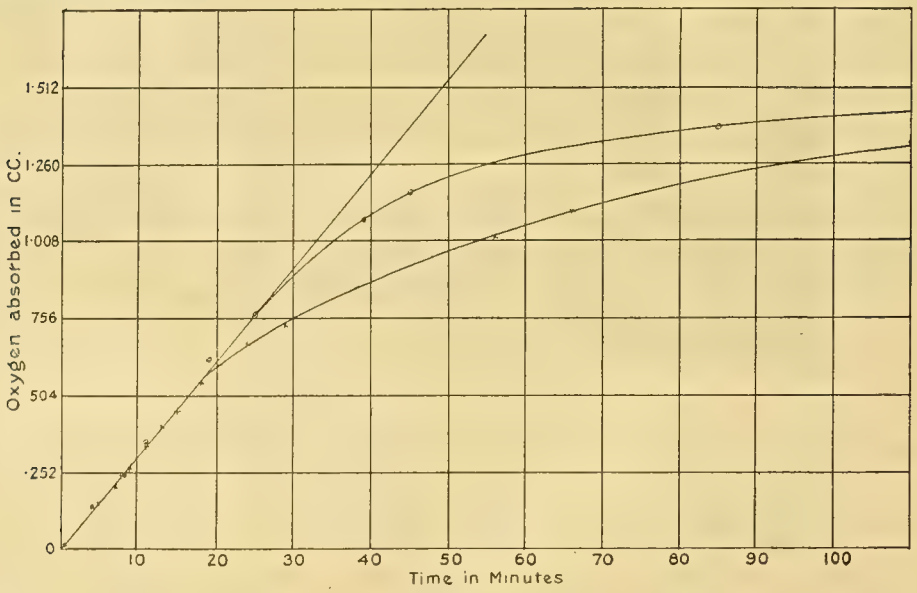

Fig. 3.

The graph, fig. 3, shows the course of the absorption. During the first part of the absorption the water is completely de-aerated by the excess

of ferrous hydrate, and, consequently, the oxygen is absorbed at a constant rate, as shown by the fact that the graph at this portion is practically a straight line. In the second stage, when all the ferrous hydrate has been oxidized, the absorption falls off gradually, so that the graph becomes a logarithmic curve. During this stage the water becomes completely re-aerated. In the figure, the second graph shows a more gradual approach to saturation than the first; this is due to the fact that during this experiment the speed of the motor driving the stirrer varied suddenly owing to variation in the voltage of the supply. This observation indicated the advisability of determining the time necessary to attain equilibrium under certain conditions. As this was intimately connected with some work which had been done previously on the rate of solution of gases by water, it was considered worth while to examine it more fully.

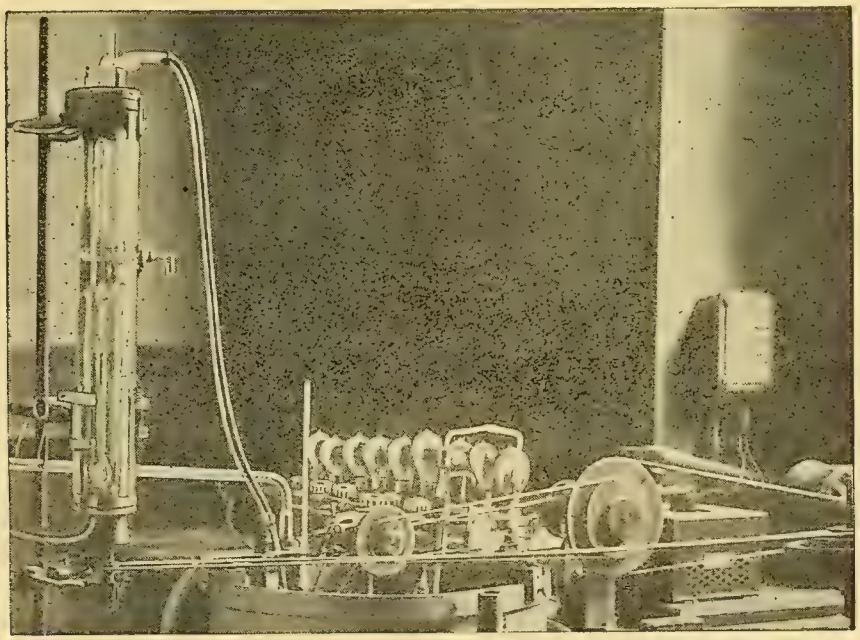

Fig. 4.

V.—Experiments on the Effect of Stirring on the Rate of Solution of Oxygen in Water.

The method consisted in introducing into the apparatus known amounts of a solution of ferrous sulphate and precipitating the hydrate by means of a solution of caustic potash; the stirrer was then driven at certain definite speeds by means of a small alternating-current motor (which could be relied upon not to vary in speed to any large extent), and the rate at which the oxygen was absorbed noted by observing the manometer.

The complete apparatus used for these experiments is shown in the photograph (fig. 4). The motor at the right of the picture drives the small circulating pump (which is immersed in the water in the thermostat), and also a stirrer in the thermostat. The water is pumped along the horizontal glass tube to the left, and into the water-jacket of the apparatus already described, from which it returns to the thermostat by the rubber tube from the top.

To the extreme right will be seen one of a series of horizontal pulleys which were connected to the small alternating current motor in order to give the desired variation in speed of stirring. This pulley is connected to the stirrer of the apparatus by the long belt appearing in the foreground, thus imparting motion to the stirrer at a rate which could be determined by the ratio of the various pulleys. The water circulation was continued, and the stirrer run at a constant speed during the course of each experiment.

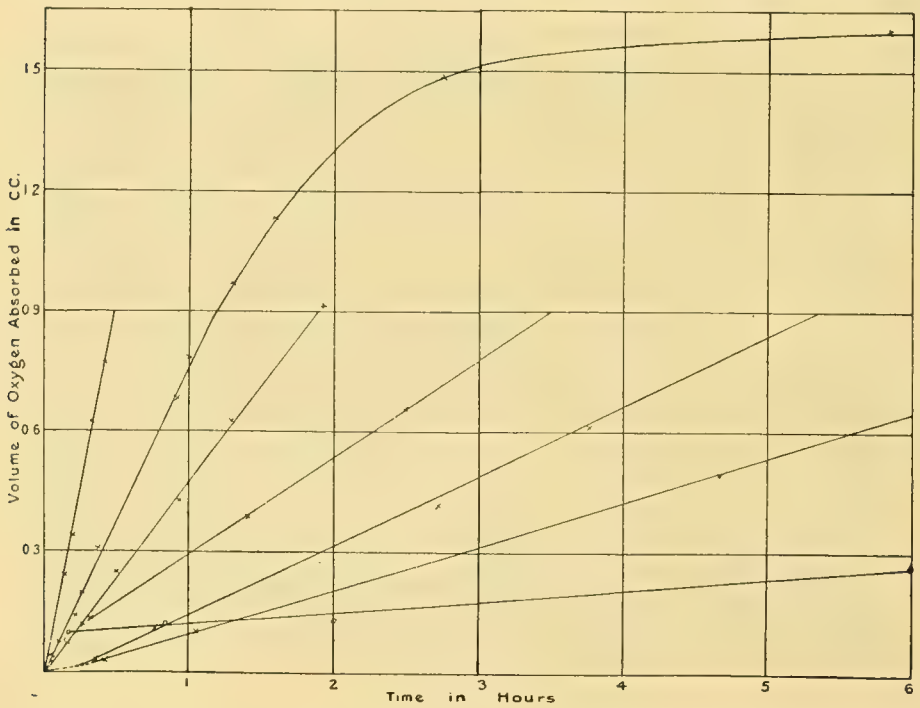

Fig. 5.

The lower speeds of revolution were counted directly, using a stop-watch to check the time, and for the higher speeds the rate of one of the slower moving pulleys was found and that of the stirrer by calculation.

Five experiments were made with different rates of stirring, and one experiment was made to compare the rate at which quiescent water absorbs oxygen with the rates at which the thoroughly stirred water absorbs it. The results of these experiments are shown in fig. 5.

The rate of stirring in these experiments varied from zero to about 1,000 revolutions per minute. The lower rates up to about 140 revolutions per minute did not appreciably distort the surface of the water, but above this speed the surface varied in shape and area with each variation in the speed of the stirrer. The shapes assumed by the water surface are shown in fig. 6; and it will be seen that they range from the nearly flat surface of still water to the point at which the air is drawn down into the water in small bubbles. At this point the surface area becomes uncertain, so that no conclusions can be drawn from experiments at higher speeds. In the other cases the surface area was taken to be approximately equal to that of a cone with the vertical axis equal in depth to that attained by the lowest point of the water surface.

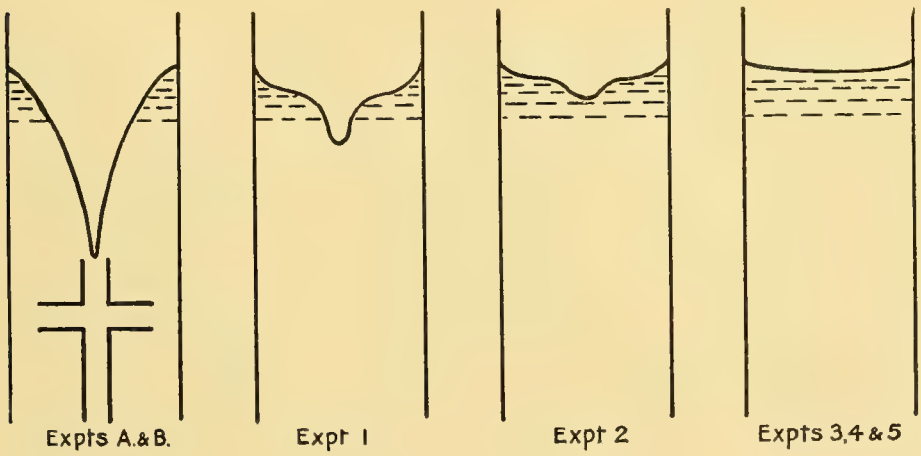

Fig. 6.

The progress of the absorption followed a linear law, as will be seen from the graph, fig. 5, and this shows that the ferrous hydrate de-oxygenated the water completely almost at once, so that the rate of solution of the oxygen remained constant until all the hydrate was oxidized.

The variation in the value of the rate of solution with stirring is shown in the table and in fig. 7. On the graph the lower line shows the rate of solution under the conditions of the experiment plotted against rate of stirring, and the points lie approximately on a straight line. Hence under the conditions of these experiments the rate of solution varies directly as the rate of stirring.

Values of Rate of Solution for different Rates of Stirring.

Experiment.	Speed of Stirrer, r. p. m.	Estimated Areas of Surface, sq. cm.	Rate of Solution in c.c. per min.	Rate of Solution per unit area. $S = \frac{a}{A}$.
A and B.	1000	19·0	·030	·0016
1	590	11·1	·014	·0013
2	340	8·8	·008	·0009
3	140	8·1	·004	·0005
4	80	8·1	·003	·0004
5	60	8·1	·002	·00025
6	0	8·1	·0001	·00001

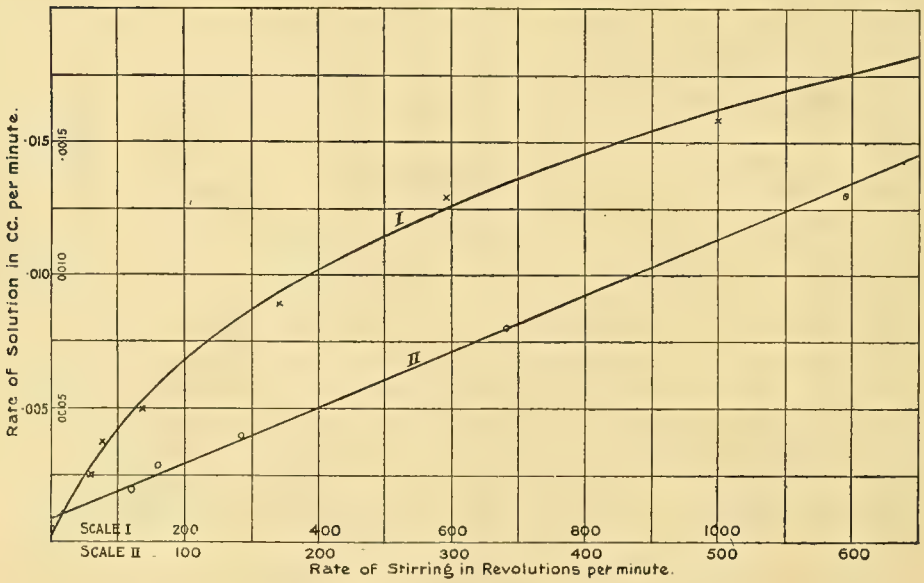

Fig. 7.

When, however, the effect of increased surface area is taken into account, and the rate of solution per unit area plotted against rate of stirring, the result is the upper line in fig. 7. This curve shows the rapid increase in the rate of solution at first, which gradually falls off as the higher values are reached, and tends to reach a maximum.

VI.—COMPARISON OF RESULTS.

The results obtained in Experiment 6 are shown as a graph in fig. 8 in order to afford a comparison between the rate at which the oxygen is absorbed by quiescent water and the rate when the water is stirred. The water was at first stirred for two minutes in order to mix the ferrous hydrate with the liquid, and thus reduce the oxygen content to zero. During this period the rate of absorption was of the same order as obtained in the other experiments. The stirring was then stopped, and the rate fell off slowly as the liquid came to rest until it reached a value which remained nearly constant for three days. On the third day this suddenly changed for a higher value, which remained constant until the sixth day, by which time only about half the saturation value had been reached. The liquid was then stirred again, and the remainder of the absorption was completed in about five hours. Hence a process of absorption which may take many days to complete when the water is quiescent takes place in as many hours with moderate stirring.

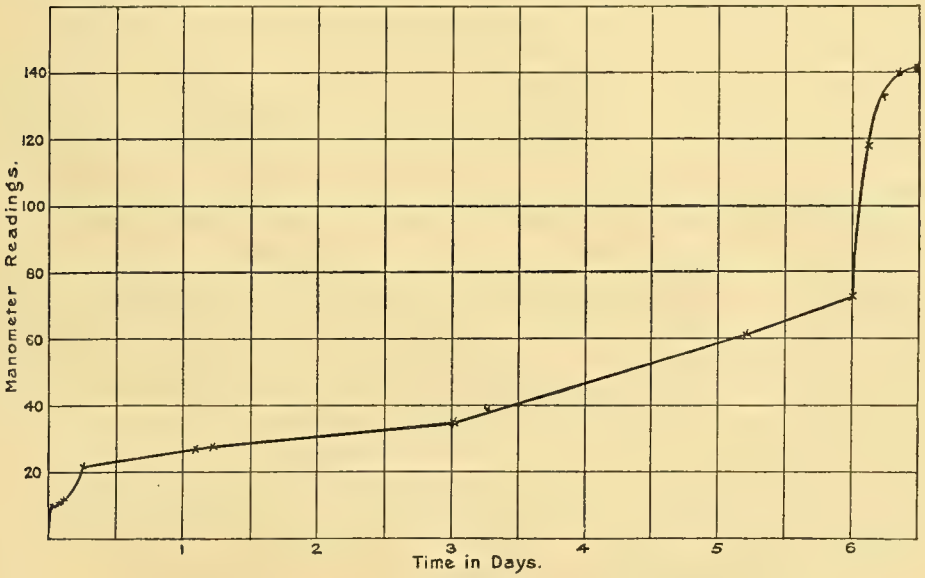

Fig. 8.

The sudden change in the rate of solution of oxygen by the quiescent water indicated above is characteristic of the process under these conditions, for the rate of solution of gases by water is then liable to sudden and unaccountable variations within narrow limits.

The greatest value for the rate of solution per unit area given in the table represents the maximum rate attainable under the conditions of these

experiments, without allowing the surface exposed to become indefinite : hence it is of interest to compare this with the rate of solution as determined in previous experiments.[1]

The rate of solution of oxygen into air-free water has been found by a totally different method to be ·0161 c.c. per minute per square centimetre of area exposed. Hence for the oxygen in the atmosphere the rate should be $\cdot0161 \times \frac{21}{100} = \cdot0034$ c.c. per minute under similar conditions, since the rate of solution has been shown to be proportional to the partial pressure.

This value is more than twice as great as the maximum value attained in these experiments (·0016), showing that the rate of mixing that was reached under these circumstances was not so rapid as that obtaining in the experiments referred to. This was to be expected, since in those experiments the water was exposed to the oxygen in very thin layers, and very perfectly mixed immediately afterwards. However, the fact that the two values come so near each other shows that with more perfect stirring arrangements it might be possible to approximate very closely to the maximum rate of solution.

These experiments therefore afford a connecting link between the conditions obtaining in the work referred to and those obtaining in nature. They also emphasize the important part played by mixing of the water in determining the rate of solution. It will be seen on reference to the table that very gentle stirring of the under layers of the water increases the rate of solution as much as twenty-fold as compared with stationary water. This bears out the view put forward previously,[2] that the rate of solution of air by water under ordinary conditions is largely determined by the rate of mixing. Experiments are being continued with this apparatus; and it is hoped to publish further results in the future.

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[1] Adeney and Becker: Scientific Proc. R.D.S., xv, p. 625. 1919.
[2] Adeney and Becker: Scientific Proc. R.D.S., xvi, p. 143. 1920.

XXVIII.

THE OCCURRENCE OF A SEQUOIA AT WASHING BAY.

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AND
JANE G. GILMORE, B.Sc.

[Plates XIII, XIV.]

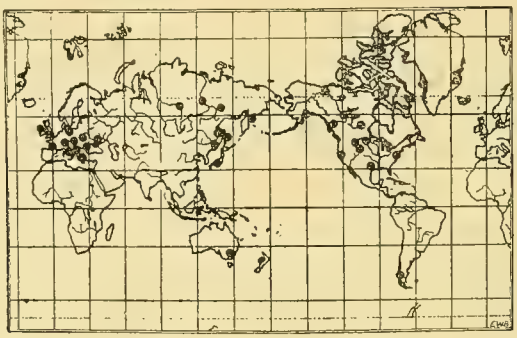
Read June 28. Published August 29, 1921.

In the course of examination of the Washing Bay core we have met with not only isolated seeds and pollen-grains of the genus *Sequoia*, the only Conifer found in it, but fortunately foliage shoots and cone-bearing twigs also, enabling us to identify the fossil.

Sequoia (or Wellingtonia) has a very limited present-day geographical range, being confined to the west Pacific coast of North California (and Oregon). One species, *S. sempervirens* (Sargent) (1), the Redwood, grows on sandstone to the height of 400 feet and a diameter of 28 feet, exposed to the warm Pacific winds and fogs, mainly in a mountain forest belt along the coast of California; it ascends to 3,000 feet, and rarely occurs inland more than 20 miles. *Sequoia gigantea* or *Sequoia Wellingtonia* (1) (Sargent sp.), the Mammoth tree, the other living species, grows between 36°–39° N., on the western slopes of the Sierra Nevada, up to elevations of 8,000 feet, lives to 4,000 years of age, reaches a height of 320 feet or more, and a diameter of 35 feet.

Though now recognized as one of the wonders of nature, the first-named of these giants of the forest was not discovered until 1847, a date it is well to keep in mind in criticizing the Conifer identifications of the earlier palaeobotanists (e.g., of the Mull plants). It is generally agreed that *Sequoia*, the only member of the family Sequoiineae, is a very ancient genus, and represents one of the earliest families of Conifers. It has been traced, at any rate, to the earliest Cretaceous beds, increasing in frequency and variety of form into the Miocene, in which it is represented by many species. It was one of the many circumpolar or Arctic genera which radiated southwards during the Cretaceous and early Tertiary epochs. Like many other genera now confined

to North America or to East Asia, it flourished at one time in Europe, and fell before a lowered temperature and other adverse conditions. C. and E. M. Reid (2) describe and illustrate a cone from the Pliocene beds on the Dutch-German border as probably the last trace of *Sequoia* in Europe. E. W. Berry (3) gives a useful map (fig. 1) showing the almost world-wide distribution of *Sequoia* during the Tertiary epoch, in striking contrast to its present restricted area. Its occurrence in New Zealand, South-East Australia, and South America, the only localities recorded by him in the Southern Hemisphere, is worthy of note, and seems in need of critical confirmation. West and Central Europe, North-East Asia, North America, and the Arctic regions were its chief centres.



Sketch Map showing the location of Caenozoic records of *Sequoia*.
After Berry, from "The Plant World."

It will be well to state here the distinguishing characters of the foliage of the living species of *Sequoia* for comparison with fossil forms. In both species the leaves are mostly spirally arranged, and more or less clearly decurrent. In *S. sempervirens* the base of the leaf is so twisted that the leaves appear distichously arranged. They are yew-like, linear, and flattened, with a single vein as midrib. The apex may be acute or obtuse. In *S. gigantea* the spiral arrangement is undisturbed and obvious, the leaves narrow and subulate, roughly three- or four-sided (rhomboidal), with one vein. They are more or less adnate or adpressed in their lower part, spreading above. Their ridged bases are so decurrent and close together as to cover the whole surface of the stem, thus leaving no part of the stem surface proper exposed. Further, in both species there are small ovate-triangular, squamiform, keeled, closely adpressed, spirally arranged leaves. Thus both species are dimorphic. The squamiform leaves occur on the cone-bearing shoots in both species, and at intervals on the foliage shoots of *S. gigantea*. They occur in *S. sempervirens* also at the tips of the foliage shoots, making its buds "scaly" in contrast to

the "naked" buds of *S. gigantea*. They also occur at the bases of the foliage shoots of *S. sempervirens*, being in reality the persistent bud-scales through which the foliage shoot has grown and elongated. S. Gardner (4) notes the interesting fact that when introduced into a warmer climate, such as that of Madeira, *S. sempervirens* develops more of these leaves, an indication apparently of more vigorous growth in a warmer climate, with consequent formation of bigger buds. This may indicate that adpressed foliage is more adapted than the spreading foliage to a warmer climate. A reduction of transpiration and an exposure of one side only to sunlight, if bright, are obvious advantages of adpression. One would expect such foliage in ancestral *Sequoias* growing in the tropical or subtropical conditions of the Cretaceous or early Tertiary. It is the prevailing type in our *Sequoia* and in that of Bovey Tracey (5). We hope to prove that the *Sequoia* found in the two localities is identical, and the beds containing it contemporaneous, viz., *Sequoia Couttsiae* Heer in the Upper Oligocene.

As already mentioned and as our illustrations (Pl. XIII, figs. 1–9) show, *S. Couttsiae* Heer possesses in the main an adpressed foliage. The leaves are semi-ovate or triangular, imbricate, decurrent, more or less falcate, with acute apex, and are spirally arranged. Each leaf is keeled or ribbed in correspondence with its solitary vascular bundle. One frequently finds at the tip of the leaf a sharp-pointed brittle cap of amber (Pl. XIII, fig. 10), which has evidently oozed out from the single resin-passage known to occur in the leaves of recent *Sequoias*. Under the dissecting microscope one can detach the amber tip and leave the leaf apex blunter in consequence.

The leaves are readily restored. Stomata (Pl. XIII, figs. 11–12) occur on both surfaces, and on the lower side form two bands, one on either side of the midrib. With a view to testing the taxonomic value of the arrangement and character of the stomata, we made a series of preparations of the leaf of living *Sequoia* and other Conifers.

C. and E. M. Reid (6) were able by restoration of the epidermis of the Bovey Tracey material to show that Heer's species was rightly named; that it was a *Sequoia*, and not, as S. Gardner stated, an *Athrotaxis*. It needs little knowledge of the Conifers to make one realize the helplessness of positive identification based on the external characters only of the foliage, owing to its pronounced heteromorphism. With differences of form supported by difference of microscopic characters there is more hope of success. A reliable way of distinguishing *Sequoia gigantea* from *Cryptomeria japonica* and *S. sempervirens*, and *S. Langsdorfii* from *Taxodium distichum* microscopically would be distinctly helpful. Bertrand (7) could find no difference in the epidermis of *Sequoia* and *Cryptomeria* in the distribution or arrangement of

the stomata or in the structure of the epidermis. We find, however, a marked difference in the size of the stomata. Those of *Sequoia* are 56–64μ long; those of *Cryptomeria* only 40–46μ in our material. If this difference held good in general, it would be a useful means of discrimination. The following table gives the results of measurement of the length of the stomata:—

	μ
Sequoia gigantea, ...	56–64
„ sempervirens, ...	56–64
„ Couttsiae, ...	52–66
„ "du Noyeri,"	48–60
(Cryptomerites du Noyeri Seward)	
Taxodium distichum, ...	46–56
* „ mucronatum, ...	46–56
Cryptomeria japonica, ...	36–46
*Glyptostrobus heterophyllus (South China), .	40–46
* „ „ (Hong Kong), .	54–62
*Taiwania cryptomerioides, ...	56–66
Athrotaxis laxifolia, ...	36–44

It will be seen that the fossils referred to *Sequoia* agree with the living species of the genus, their smallest stomata being larger than the largest ones of *Cryptomeria*.

The *Glyptostrobus* measurements seem to cast doubt on the taxonomic value of the size and arrangement of the stomata. Those in the specimen from South China, showing spreading yew-like foliage, lie parallel to the long axis of the leaf, and are of the size of those of *Cryptomeria* in contrast to those in the Hong Kong specimens, with adpressed foliage, which, though on the whole parallel to the long axis, are less regularly arranged, and of a size comparable to those of *Sequoia*.

While in most of the species listed stomata occur on both upper and under surface of the leaf, in *Athrotaxis laxifolia* they are confined to the upper surface. The stomata on the under side of a leaf generally form two bands or ribbons parallel to the midrib. In the ribbon one may see in many cases distinct rows or files of stomata. When the leaf is decurrent the bands can be traced on to the stem. These "stem" stomatal bands are particularly well marked in *Glyptostrobus*. In *Sequoia* the individual stomata lie with their long axis for the most part parallel to the midrib; in *Cryptomeria* they are more irregularly arranged. Florin, who has investigated the epidermal

* We are indebted to Professor A. Henry for this material.

structure of the leaf of a number of Conifers, citing Mahlert in support, notes that in *S. gigantea* all the stomata lie with their longitudinal axis parallel to the direction of the bundle, while in *S. sempervirens* numerous transitional positions also occur. In our investigation of *Sequoia*, before we had Florin's results, we found that, while the stomata in *S. sempervirens* lie parallel to the midrib in the normal spreading foliage, they are less regularly arranged in the leaves of its fertile shoots, and in the general foliage of *S. gigantea*.

Taxodium distichum shows the stomata in the two bands arranged lengthwise in series, but also transversely in rows. Each stoma, on the whole, lies with its long axis horizontally placed, i.e., at right angles to the direction of the vein. *Taxus baccata* shows stomata in vertical rows parallel to one another, the individual stomata in each vertical row looking like links in a chain, with vertical longitudinal axis. The mode of arrangement of the stomata should prove a valuable diagnostic character in distinguishing between fossil *Taxodium* and *Sequoia*, e.g., *T. distichum miocenicum* and *S. Langsdorfii*, in which we have so far failed in our attempts at restoration by maceration.

While the adpressed squamiform leaf, 2–4 mm. long, is the prevailing type in *S. Couttsiae*, narrow, acicular, or subulate, sometimes markedly divaricate leaves, 4 mm. long, also occur (Pl. XIII, figs. 6–9). We have many twigs bearing these leaves only, and were struck by their similarity to the specimens from the Interbasaltic beds of Co. Antrim, named by Baily *S. du Noyeri* (8). One specimen (Pl. XIV, fig. 1) from the Grainger collection in the Belfast Museum shows both types on the same shoot, and the resemblance to the fertile shoot of *S. gigantea* is marked. The type specimen of *S. du Noyeri* Baily (Pl. XIV, fig. 2) shows impressions only, in the ironstone. As our photograph of the type shows, Baily's drawing (Pl. XIV, fig. 3) makes the leaf much too long. This figure may have led Gardner to conclude that *S. du Noyeri* was really a *Cryptomeria*. We are of opinion that it is a *Sequoia* and, at the most, a form of *S. Couttsiae*.

It is clear from Saporta's illustrated account of *S. Couttsiae* var. *polymorpha*, that a form of *S. Couttsiae* grew in the south-east of France not unlike the *du Noyeri* form of *S. Couttsiae* in north of Ireland, the Baltic region, and Greenland.

If Gardner's drawings of cones of the Glenarm material are correct, then we must admit that *Cryptomeria*, now confined to China and Japan, grew in Co. Antrim in the Tertiary. It is not, however, recorded elsewhere in the fossil state. We have restored the epidermis of the leaf of a Conifer from Glenarm. It has all the characters of a *Sequoia*. In the same slab are winged seeds (Pl. XIV, fig. 13) indistinguishable from those of *S. Couttsiae*,

and unlike the almost wingless seed of *Cryptomeria*, which was evidently not, as Gardner thought, the only Conifer at Glenarm.

Pollen-grains are frequent throughout the part of the core examined. They are spherical, finely punctate, 25–31μ in diameter, and agree with the fresh pollen-grains of *S. gigantea*. More than once bodies like Pl. XIV, fig 4, occur, indicating a pollen mother cell in course of division. They may or may not belong to *Sequoia*. The branching shoot shown in Pl. XIV, fig. 5, is interesting, but, without breaking it up, it is difficult to decide as to the nature of the two swollen terminal buds. They may be scaly foliage buds, male flowers, or even young cones. No signs of pollen-grains were obtained by examination of the restored counterpart. Cones, however, occur, as well as isolated seeds, and we had the good fortune to find one cone split open—borne on a shoot carrying true *S. Couttsiae* leaves (Pl. XIV, figs. 6–7)—in such a way as to show its structure as clearly as if it were a median section of a fresh cone. Several seed-bearing scales are exposed. Seeds (Pl. XIV, figs. 7–10) are observable on the upper surface of each scale, overlapping one another, being inverted or pendulous, 3·5 mm. long, 2·7 mm. broad at the base. Each seed shows a central somewhat curved "nucleus," with two fairly broad lateral wings. The seed is pointed or apiculate at its lower or micropylar end, broader and emarginate at its upper basal attached end. The hilum as a disc-like scar is clearly observable. The seeds are attached at the distal end of the ovuliferous or bract scale. A casual inspection of Sargent's figures of the seed scales in the two living *Sequoia* will suffice to show a marked difference in the arrangement of the seeds in the two. It is worthy of note that *S. Couttsiae* agrees with *S. sempervirens*, and not with *S. gigantea*, in the size and structure of its cone and arrangement of its seeds. The main (adpressed) type of foliage of *S. Couttsiae* is strictly localized in *S. sempervirens*, and only here and there observable in *S. gigantea*; otherwise it is buried in the past. It may be added that the cone of *S. sempervirens* ripens in one season, but, according to Sargent, that of *S. gigantea* ripens in the second season, as in *Pinus* and other Abietineae.

There is a certain amount of lignite in the core, and some of our preparations show typical Conifer tracheides, with a single row of bordered pits (Pl. XIV, fig. 10) on their radial walls, much as in recent *Sequoia* wood. We hope to make a more thorough examination of the lignite later. As *Sequoia* and *Taxodium* are usually associated with lignite deposits, a second boring might reveal larger deposits of lignite, giving a fuel capable of utilization in the baking of the enormous thickness of clay which makes, we understand, a satisfactory, though coarse, kind of pottery.

S. Couttsiae Heer seems to have suffered a good deal at the hands of investigators. Heer's drawings, supplemented by the photographic illustrations of C. and E. M. Reid, leave one in no doubt of the general characters of the species. Heer gives a figure (*op. cit.*, fig. 12) of *S. Couttsiae* showing linear leaves, longer and more divaricate than usual, but he shows in fig. 9 the transition to the normal type. He clearly realized the dimorphism of *S. Couttsiae.* We have before us material from Bovey (Pl. XIV, fig. 11) (Reid Collection, York Museum), Co. Antrim (Grainger Collection, Belfast Museum) (Pl. XIV, fig. 1), Disco (Dublin Museum) (Pl. XIV, fig. 12), as well as Baily's type specimen of *S. du Noyeri* (I. G. Survey) (Pl. XIV, fig. 2). We are of opinion that *S. Couttsiae* Heer was common to Greenland, Ireland, and Devonshire, and that *S. du Noyeri* Baily and *S. Whymperi* Gardner should be treated as synonyms.

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EXPLANATION OF PLATES.

Plate XIII.

Figs.

1–9. Branches of *Sequoia Couttsiae* from Washing Bay.

1–5. Shoots with squamiform foliage.

1–3 are magnified. (× 3.)

6–9. Shoots showing acicular leaves, occasionally divaricating. (× 3.)

10. Resin tips of leaf. (× 80.)

11. Stomata from squamiform leaf of *S. Couttsiae.* (× 240.)

12. Stomata from acicular leaf of *S. Couttsiae.* (× 240.)

Plate XIV.

1. The two types of foliage on the same shoot of *S. Couttsiae.* (Grainger Collection, Belfast Museum.)
2. Type specimen of *S. du Noyeri* Baily. (Irish Geolog. Survey Collections.)
3. Photograph of Baily's restoration of specimen in fig. 2.
4. Pollen mother-cell dividing. *Sequoia?*
5. Branch of *S. Couttsiae* with terminal buds. Male flowers? (× 3.)
6. Cone of *S. Couttsiae.* ($\frac{1}{1}$.)
7. Scale of cone, with overlapping seeds attached. (× 8.)
8. Shoot of *Sequoia Couttsiae,* showing foliage and exposed seeds. (× 3.)
9. Isolated seed of *S. Couttsiae,* showing micropole (m) and hilum (h).
10. Tracheides, showing bordered pits.
11. Foliage of *S. Couttsiae* from Bovey Tracey. (York Museum.) (× 3.)
12. Foliage of *S. Couttsiae* from Disco Islands, Greenland. (Botanical Collections, National Museum, Dublin.) (× 3.)
13. Seed of *S. Couttsiae* from Glenarm. (× 3.)

XXIX.

THE SOURCES OF INFECTION OF POTATO TUBERS WITH THE BLIGHT FUNGUS, *PHYTOPHTHORA INFESTANS*.[1]

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[Read June 28. Published August 29, 1921.]

I.—Previous Work on the Manner of Tuber Infection.

In his important paper on the control of potato blight, Jensen[2] distinguishes between two periods during which infection of the tubers occurs. The first is while they are still *in situ* in the soil; and the decay set up by the parasite is generally obvious at digging time, or at the latest by about one week after that operation. The second occurs during lifting, a copious development of Phytophthora rot setting in about one week after the potatoes have been dug.

Jensen, if he was not the first to draw attention to the danger of digging the crop while any green foliage remains on diseased plants, appears to have been the first, at any rate, to emphasize the magnitude of the danger, to give a rational explanation of it, and to suggest a remedy.

According to this author, "si l'on arrache les pommes de terre avant que les fanes soient complètement mortes et pendant que les feuilles portent encore des quantités de spores capable de germer, ces spores vont tomber en quantité sur les tubercules . . . et une semaine après ou un peu plus tard, si la température est basse, l'effet fatal s'en fera sentir." And it is further stated: "si l'on retarde l'arrachage jusqu'à ce que les spores soient mortes, c'est à dire environ deux semaines après le dessechement des fanes, tout danger est evité."

There are quoted in support of this view the results of two experiments

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[1] Acknowledgment is made to the Department of Agriculture of the Dominion of Canada for permission to publish in advance the results of experiments carried out in that country.

[2] Jensen, J. L.: "Moyens de combattre et de détruire le Peronospora de la pomme de terre." Mém. Soc. nat. d'Agriculture de France, t. cxxxi. 1887.

in which portions of plots were dug successively on September 7th, 12th, 15th, and October 11th. The following percentages of the crop developed Phytophthora rot:—1st digging, 21·5; 2nd digging, 33·5; 3rd digging, 13·0; and 4th digging, 0 per cent. As to the condition of the foliage during this period, it is stated that a certain amount of foliage was still green and covered with spores when digging was first begun; at the second and third diggings almost all the leaves were withered, but some spores were still present, while at the last date all the leaves and stalks were dried up. Rain which occurred during lifting was held responsible for the large percentage of rot occurring in the second lot of potatoes which were dug on September 12th.

While Jensen had reached the conclusion by experimental methods that soil to which spores had been added remained capable of causing infection for a longer period than the spores themselves continued to be viable while still on the leaves, and that in fact spores which had actually fallen to the ground might prove sources of infection to the tubers during the operation of digging, he over-estimated the importance of infection arising directly from diseased foliage, and under-estimated the part played by contaminated soil. His final conclusion was that the crop was likely to decay in storage if it was dug too soon, "c'est à dire pendant que les spores se trouvaient encore dans les feuilles."

To his belief in this theory is traceable the inconsistency noticeable in the practical directions which he gives for the control of tuber rot after digging. Thus, he found experimentally that only about 1 per cent. of the spores produced on the leaves survived a dry day; and that soil with which spores had been mingled induced rot in potato slices up to five days afterwards, indicating a length of spore life of five days in the soil. In spite of these results it was found necessary in practice to refrain from digging for as long as two weeks after the complete drying of the foliage. Nevertheless, he believed that where it was not possible to delay digging sufficiently long to allow an interval of even five or six days after the removal of the stalks, the danger could be considerably reduced by such precautions as refraining from digging during rain, beginning work at the windward side of the field, digging in the afternoon rather than in the morning, and especially by removing the stalks, even though digging was to follow immediately. An experimental basis for the latter conclusions, which suggest an ephemeral character for the spores of the fungus, and neglect the possibility of infection from contaminated soil, is not given.

Jensen's conclusions as to the danger of digging the crop while the foliage is blighted were tested experimentally in the United States by Jones and

Morse.[1] The results are summarized by Jones, Giddings, and Lutman[2] as follows :—" . . . where the tops are attacked by the late blight the harvesting of the tubers should be delayed until a week or more after the death of the tops." In the results of two experiments quoted 55·3 per cent. and 18·4 per cent. of the potatoes rotted when they were dug early, while the percentages of rot in similar potatoes dug from three to four weeks later were 7·3 and 6·0 respectively. The condition of the foliage as regards blight was not stated.

Jones and his co-workers did not go into the question of the source of tuber infection after the foliage was practically or completely dead, although they seemed to have assumed that such infection was possible. Jensen proved that the spores remained viable for five days in soil, but his work necessitates the assumption that tubers may contract the disease during more than double that period after the foliage is dead. If this actually takes place, it is necessary to assume an unsuspected amount of vitality in the spores of *Phytophthora infestans* or the existence of some hitherto undiscovered phase in the life-history of the fungus.

II.—PHYTOPHTHORA TUBER-ROT IN EASTERN CANADA.

The present author was led to a consideration of the question of the sources of tuber infection by residence for some years in the Maritime Provinces of Canada, where the ravages of blight developing in the tubers after the crop is dug sometimes exceed the damage wrought by the disease on the growing crop. A considerable number of blighted tubers are sometimes found when the crop is lifted, yet at other times such tubers may be almost absent. When, however, the apparently healthy portion of the crop is stored, in many cases an outbreak of Phytophthora rot sets in which may destroy a large proportion of the tubers. In some cases the result is that not the one-twentieth part (or thereabouts) of the normal crop required to supply "seed" for the following year survives. The sale of tubers may be almost entirely held up for a month or two in the autumn in bad years, because buyers are afraid to touch any potatoes, no matter how sound they look. After the latter part of October the danger is held to be over, as the disease will by then have developed far enough to be recognized.

[1] Jones, L. R., and W. J. Morse: "Potato Diseases and their Remedies.—Relation of date of digging to development of rot." Vermont Agr. Experiment Station, Fifteenth Annual Report (1901–2), pp. 219–223, 1902 ; Sixteenth Annual Report (1902–3), pp.161–162, 1903 ; Seventeenth Annual Report (1903–4), pp. 391–395, 1905.

[2] Jones, L. R., N. J. Giddings, and B. F. Lutman : "Investigations of the Potato Fungus, *Phytophthora infestans*." U.S. Dept. of Agriculture, Bureau of Plant Industry, Bull. 245. 1912.

The reason for the development of such a severe attack late in the season seems to be twofold. The climate in late summer and autumn is almost always such that blight is present, and yet in many cases a balance is maintained, so that both plant and parasite go on developing until up to, or nearly up to, digging time. There is frequently no frost in the coastal districts until late October or even early November; and the season is so short (June 1st to October 15th) that the stalks do not die from natural maturity. In the second place, some of the varieties grown there are standard American potatoes, which, as is well known, are on the whole very susceptible to blight, and are not suitable for cool coastal regions. Due to this combination of circumstances, the results about to be described have a significance for portions of Eastern Canada which is not, perhaps, equalled elsewhere; but, as will be shown, the same factors also operate in Ireland to some extent.

The observation was made in 1915, the first season spent in Canada, that a conspicuously small amount of tuber disease followed a most severe blight attack, which completely killed all the foliage early in September. As it turned out, this was the most serious blight epidemic which occurred in the five-year period 1915–1919, yet the amount of tuber rot which followed was far lower than in any of the other years mentioned. The total amount of Phytophthora tuber rot developed by the crop in that season, including that found in storage up to the following April, was only 1·2 per cent., while the corresponding average for the succeeding four years[1] was 26·3 per cent. In none of the latter years was the blight sufficiently severe as a rule to kill the foliage completely before the crop was dug. The attack, therefore, persisted longer, to which fact is generally attributed the greater amount of decay in the tubers, because of their being exposed to infection for a greater length of time.

It is generally agreed that a long period of spore discharge (that is, a moderate and long-continued attack of blight) and severe tuber rot are associated; and the prevalent view is that the latter is a direct consequence of the former. The assumption must then be made that more spores find their way to the soil when the blight never (or certainly not for a long time) develops sufficient intensity to kill the plants, than happens when the blight attack is much more severe but less protracted; or, alternatively, that under the former conditions the spores reach the tubers in greater numbers or under more favourable conditions for infection. These are hypotheses which

[1] The figures for 1919 do not record the amount of tuber rot developed after November, but they include the severe outbreak which generally occurs within the first month after harvesting, subsequently to which little or none develops.

should be susceptible of experimental proof, but this has not been forthcoming up to the present.

In the case of protracted blight attacks late in the season it is important to distinguish between tubers in which the disease appears at, or soon after, the time of digging and those which develop disease some time after having been stored. Both outbreaks are often similarly explained (or, rather, are not distinguished), it being held that infection is in all instances contracted while the tubers are still *in situ* in the soil. At other times the appearance of large amounts of disease some time after digging is explained by the assumption that the disease spreads from tubers originally infected in the field to their neighbours during storage in pits and other places.

Evidence will be presented to show that the great bulk of the tubers which develop Phytophthora rot subsequent to digging were not already infected in the soil while still attached to the plant, and do not become infected in storage from contact with other tubers so attacked, but that, in fact, a distinction must be drawn between the ordinary course of infection (which may be called "subterranean infection") and another method, which, for want of a better term, may be called "surface infection." The distinction is, theoretically, not very far-reaching, but for practical purposes it is of much importance.

III.—Tuber Disease in Canada following Early Cessation of Spraying.

A further opportunity occurred in 1917 of testing the conclusion arrived at two years before, namely, that any circumstance which preserves the foliage until late in the season but then allows it to become partially blighted increases the amount of disease in the tubers. Owing to conditions over which sufficient control was not possible, a succession of sprayings was concluded nearly one month before the normal time on an experimental area of one acre of potatoes. The field was divided into twelve plots, of which three received no treatment, three were sprayed four times, three others three times, two plots twice, and one once. It was intended that certain of the plots should receive two further applications, but these were omitted. After spraying operations ceased the blight became serious, but the haulms in all the plots survived in part until October 3rd, when the potatoes were dug. The control plots were an exception, for they were most severely blighted and had been practically dead for some time. The results are given in Table I.

TABLE I.

Development of Phytophthora rot in sprayed and unsprayed potatoes in Prince Edward Island, Canada.

No. of applications of spray.	Percentage by weight of blighted tubers.			
	In the field.	In storage to Nov. 30.	In storage to April.	Total.
4	1·6	13·0	0·4	15·0
3	1·9	23·0	2·4	27·3
0	7·2	4·8	0·0	12·0
2	3·3	12·0	0·3	15·6
1	6·0	10·5	0·0	16·5
0	3·2	3·3	0·3	6·8
4	1·0	10·8	2·9	14·7
4	2·1	21·2	0·0	23·3
0	9·6	4·6	0·0	14·2
3	3·7	11·7	0·7	16·1
3	3·7	17·0	3·0	23·7
2	5·7	8·7	0·0	14·4
Average sprayed,	3·2	14·2	1·1	18·5
Average unsprayed,	6·7	4·2	0·1	11·0

It is evident that the sprayed plots (which, incidentally, gave an increased yield) showed a considerable reduction in the amount of diseased tubers, the average for the untreated plots being 6·7 per cent., and that for all the sprayed plots 3·2 per cent. The crop from each plot was placed separately in a storage cellar, and the potatoes were again sorted at the end of November. The result was then reversed, the potatoes from the sprayed plots showing on the average more than three times as much disease as those which had no treatment. This result was comparatively uniform throughout all the twelve plots, and, on the whole, the potatoes which were sprayed oftenest had the greatest amount of tuber rot, those sprayed less often had less, and the unsprayed plots had considerably the least. So great was the amount of disease which appeared after the potatoes were stored that it much more than neutralized the original advantage (so far as tuber disease is concerned) resulting from spraying.

A practically identical result was obtained from another acre plot in the same year (1917) which had similar treatment. The two last applications of spray had to be omitted on half the field (four plots), while the other four plots, which alternated with the first, were left untreated. There were somewhat more diseased tubers in the unsprayed plots when the crop was dug, but relatively much less after it was stored. The figures available give the amount of disease up to November 30th only, when the total for the unsprayed potatoes amounted to 12·7 per cent., while that for the sprayed potatoes reached 27·7 per cent.

These results seemed again to show that more tuber disease might follow a less severe, if more protracted, attack of blight. An examination of the results does not, however, support the view that the amount of tuber rot is a function of the length of the period of spore production.

The sprayed plots in which the disease lasted longest on the foliage showed the smallest amount of disease in the tubers at the time when the crop was dug. On the other hand, the potatoes from these plots developed a far greater percentage of the disease during the subsequent two months' storage. It is possible that the disease which became evident some time after digging was contracted before that operation, but that the rot had not advanced sufficiently to be visible. A direct answer to this objection cannot be given, because, unfortunately, the interval which elapsed between digging and the advent of the bulk of the tuber disease is not known. The supposition, however, is an improbable one.

When a potato tuber becomes infected with blight, visible evidence of infection under field conditions appears in about a week. That being so, all the disease is visible on potatoes dug on any particular date except that contracted, approximately, during the previous seven days. When, as frequently happens, a serious outbreak of tuber disease follows at an interval after harvesting, it presupposes, if this hypothesis be tenable, a remarkable increase in the amount of infection in the week immediately previous to digging—an increase which is difficult to explain. There is no evidence to support the suggestion of Jones and Morse,[1] that early digging favours the *development* of the parasite in the tubers, with the result that rot follows, while in the case of potatoes dug later the fungus, though present, remains dormant.

On the other hand, the great increase in the amount of tuber rot following after harvesting may, perhaps, be more reasonably connected with the changed

[1] Jones, L. R., and W. J. Morse: "The Relation of Date of Digging Potatoes to the Development of the Rot." Proc. 25th Ann. Meeting of Soc. for Promotion of Agricultural Science, pp. 91–95. 1904.

conditions as regards exposure to infection brought about by the actual lifting of the crop. To attempt to decide between these alternatives, three series of experiments were carried out in the subsequent two years.

IV.—Field Experiments on the Sources of Tuber Infection in Canada.

In an experiment carried out in 1918 the theory that storage rot originates from the contact of tubers with diseased foliage, or with surface soil within five days after it becomes contaminated, was tested in two ways. The stalks, then somewhat blighted, were removed from certain plots and the potatoes were not dug until a period of five days in one case, and eleven days in another, had elapsed. Other plots in which the foliage had been allowed to remain were dug at the same time. The second test devised consisted of digging two series of plots while the leaves were considerably blighted, and immediately treating the potatoes from one series with dilute formaldehyde solution so as to prevent further infection. All the plots were laid out in duplicate.

It is not necessary to go into the details of this experiment here, since the results were inconclusive for a number of reasons. The formaldehyde treatment, from which much was hoped, was apparently too drastic; for serious injury to the tubers, involving complications in decay, resulted. Furthermore, neither interval which was allowed between the removal of the stalks and the digging of the crop (five and eleven days) prevented a large amount of blight rot in storage. If there was anything in soil infection, it seemed as though a longer period must be allowed to elapse to render the crop safe. On the whole, however, the work appeared to be on the right lines. There was least disease in the potatoes treated with formaldehyde, and most in the tubers from those plots which were dug early and while the foliage was still blighted.

Profiting by this experience, two modified experiments were conducted in 1919. These are referred to as experiments A and B. In experiment A the efficacy of leaving a period of six days between the removal of the stalks and the digging of the crop was tested. In experiment B a much longer period was allowed—namely, thirty-four days. One experiment was carried out in quadruplicate and the other in triplicate. The average results are shown in Tables II and III.

TABLE II.

Experiment A (1919) *on the digging of potatoes at the Experimental Station, Charlottetown, Prince Edward Island, Canada.*

Plot.	Stalks allowed to stand until— (represented by ———) / Potatoes left undug until— (represented by .....)	Remarks.	Percentage weight of crop blighted. In field.	To Nov., 1919.	Total.	Net weight sound potatoes in Nov. Avg., 4 plots. lb.
—	Date of Digging, Sept. 20 / Sept. 24 / Sept. 30 / Oct. 1 / Oct. 21	—	—	—	—	—
1	———	—	0·0	35·4	35·4	69
2	———	—	0·0	4·0	4·0	112
3	———	Stored at once.	0·0	40·4	40·4	76
4	———	Tubers left on ground all day.	0·0	68·3	68·3	42
7	———	Dug after frost: stored at once.	26·7	17·1	43·8	72
8	———	Tubers left on ground all day.	23·1	21·6	44·7	66

TABLE III.

Experiment B (1919) *on the digging of potatoes at the Experimental Station, Charlottetown, Prince Edward Island, Canada.*

Plot.	Stalks allowed to stand until— (represented by ———) / Potatoes left undug until— (represented by .....)	Remarks.	Percentage weight of crop blighted. In field.	To Nov., 1919.	Total.	Net weight sound potatoes in Nov. Avg., 3 plots. lb.
—	Date of Digging, Sept. 18. / Sept. 27. / Oct. 22.	—	—	—	—	—
1	———	Tubers buried in soil again.	8·7	5·9	14·6	89
2	———	—	4·7	3·3	8·0	118
3	———	Soil sprayed: Bordeaux mixture	3·7	2·4	6·1	113
4	———	—	.....[1]	21·7	21·7	104
5	———	—	0·0	35·6	35·6	91
6	———	Dug after frost.	11·9	3·9	15·8	123

[1] A very small amount of disease found in the tubers in the field was not recorded separately, but it is included in the total.

It is clear from the first table that removing the stalks six days before harvesting is of little avail in preventing tuber infection (compare plots 1 and 3). This is so in spite of the fact that removing the stalks on September 24th reduced the length of the blight attack on the foliage by one-third. Removing the stalks ten days before digging reduced tuber infection to very small proportions. Here again, of course, the period during which blight was present on the foliage was still further diminished. It is probable that a considerable share of the success attained was due to this fact. The exact influence of each of the two factors cannot be apportioned, but it may be mentioned that a large amount of tuber infection resulted from allowing eleven days to elapse between stalk removal and digging in the experiment of 1918; and also a large amount of infection occurred in experiment B of 1919, where the interval was nine days. Ten days elapsed in the case under discussion, and while it is true that the weather conditions (which must probably be allowed to have an influence) differed in the different cases, the protection afforded to the crop is to be traced principally to the initial amount of blight present and not to the interval allowed before digging.[1]

Turning to experiment B, clear proof is obtained of the origin of Phytophthora rot in storage. The plants in plots 2, 4, and 5 retained their foliage until September 18th, when they were all moderately blighted. The last-mentioned plot was then dug at once, and the crop stored on the same day. The plants in the second and fourth plots had all their foliage removed, and one was dug nine days and the other thirty-four days later. It will be noted that the period of the blight attack was the same length in all. Notwithstanding this, 35·6 per cent. of the tubers from the early-dug plot had developed blight by November, 21·7 per cent. from the intermediate one, and 8·0 per cent. from the late-dug plot. It seems impossible to escape from the conclusion that during the thirty-four-day interval the parasite lost its power of infecting the tubers, but that, on the other hand, this power persisted for at least nine days after the last spore was shed from the leaves.

As was invariably the rule in all the experiments, three in Canada and one in Ireland, the greatest amount of tuber rot developed when the crop was dug while the foliage was still suffering from blight. On the one hand this compares with a smaller amount of disease in plots, the stalks in which were removed at or about the same time as the former were dug, but the crops of which were not dug until at least two weeks later; and, on the other

[1] This and other points, such as the possibility of the soil of plots from which the stalks had been removed being contaminated by spores from neighbouring plots, and the possibility of tuber infection during storage, are discussed more fully in a forthcoming Bulletin of the Dominion of Canada Department of Agriculture, entitled "Investigations on Potato Diseases."

hand, with plots dug in the ordinary way late in the season. This is a very noteworthy point. That potatoes which were left in the ground exposed to blight infection from spores washed down into the soil for an added period varying from twenty-one to thirty-four days should decay less than potatoes not so exposed points to some incompleteness in the generally accepted theory of tuber infection.

V.—Field Experiment on the Sources of Tuber Infection in Ireland.

In view of these results it was thought advisable to try a similar experiment in Ireland. While it is probably true that storage rot is seldom, if ever, as severe in this country as in portions of Eastern Canada, nevertheless loss due to this cause is hardly ever absent, and in some cases it becomes quite serious.

Portion of a field of Up-to-Date potatoes at the Albert Agricultural College, Glasnevin, Dublin, measuring twenty-five square perches, was selected for the work. This area was divided into thirty-three equal plots. Each of the eleven methods of treatment indicated in Table IV was tried in triplicate on these plots, which were distributed as uniformly as possible over the experimental area so as to minimize inequalities in the blight and soil conditions. Different treatments were given before and after digging, as detailed in the table, the dates of digging being there indicated. Before being stored, the potatoes were most carefully sorted and all diseased and small tubers excluded (except in the case of plot 8). The remainder were stored in small pits in the open. Each pit contained about 2½ cwt. of potatoes, representing the yield of each series of three plots. The pits were made in the usual way, very slightly sunk in the ground, the potatoes being covered lightly with straw, or, in certain cases, with potato stalks. Where old stalks were purposely used for covering they were replaced with straw after a few days. All the pits were finally covered with earth. They were opened and the potatoes again examined on February 15th and 16th, 1921.

[Table IV.

TABLE IV.

Digging and pitting experiment at the Albert Agricultural College, 1920–21.

Plot.	Stalks allowed to stand until— (represented by ———) / Potatoes left undug until— (represented by .....)	Special treatment after digging (if any).	Per cent. weight found rotted when pits were opened.	
	Date of Digging, Sept. 15, 16 / Sept. 27, 28 / Oct. 9, 12 / Oct. 18		Soft rot (cause undetermined).	Blight.
1	———	None.	1·05	3·86
2	———	None.	0	0·68
3	———	None.	0·16	9·60
4	———	None.	1·16	10·04
5	———	None.	1·07	0·27
6	———	None.	0	0·10
7	———	None.	0	0·63
8	———	Covered in pit with blighted stalks.	0·33	13·16
9	———	Covered in pit with blighted stalks.	0·81	9·76
10	———	Pitted with fifty marked blighted tubers.	1·71	0·85
11	———	Spread on plot from which blighted stalks had just been removed.	0·66	0·33

The field in which the plots were situated had suffered severely from blight throughout the latter part of July and the month of August. By the beginning of September the plants in more than half of the field were practically dead, and those in the remainder were severely blighted, but still living vigorously. The experiment was carried out on this portion of the field.

The blight made little or no headway during the comparatively dry and warm period which set in about September 1st. It had progressed no further at the time of the first digging on September 15th and 16th; and it was not until just after the second digging on September 27th and 28th that, as the result of some showery weather, it began to spread again. Thereafter the disease continued to develop, although somewhat slowly, so that there was still a certain amount of living foliage left when work was completed on October 18th.

The potatoes reported as attacked by soft rot included those which were so far decayed that the original cause could not be determined. No effort at an analysis of this category was attempted because of its difficulty. Besides, the amount of this type of rot in all cases but one hardly exceeds one per cent., and the results are not materially altered by neglecting it altogether. In the case of plot 10, where it reaches its highest level, it is noteworthy that while fifty marked blighted tubers were placed in the pit only thirty-nine were recovered in a recognizable form. Some of these would have been included in the soft rot column had they not been marked. It is probable that the missing eleven are to be similarly accounted for. If this be true for the other plots also, all the rotted potatoes should be included in the blight column, in which case again no serious difference results.

Three points are clear from this experiment. The disease which was found when the pits were opened had not spread from a few initially infected tubers. The pit (No. 10) in which blighted potatoes were placed showed hardly more blight than did No. 6 pit, which contained similarly treated potatoes without the addition of any blighted specimens. There was little evidence of any disease being communicated from tuber to tuber. In most cases the potatoes surrounding the marked blighted tubers were quite sound, although in some cases the former were covered with decaying slime. It was exceptional to find marked diseased, and unmarked potatoes which had contracted disease, in contact. As the covering of the pit was not absolutely water-tight and the interior was moist, the conditions were presumably favourable for the development of blight.

The most dangerous source of infection is, according to the experiment, direct contact of the tubers with blighted foliage. Two pits were covered for some days with the blighted stalks, which were afterwards removed and replaced with straw. No. 8, which was so covered, developed 13·16 per cent. of disease, as compared with 3·86 per cent. in similarly treated, but differently covered, potatoes in pit 1, an increase of 9·3 per cent. A similar difference exists between pits 6 and 9. The latter, which was covered with diseased stalks, showed 9·76 per cent. of blight. The former, not so covered, showed 0·10 per cent., the difference being 9·66 per cent. in this case. Although it is well known that the leaves are the source of the spores which infect the tubers, the use of stalks as a temporary covering for freshly dug potatoes is still too common a practice, and, as the experiment shows, it is a most dangerous one. Had there been a vigorous development of blight on the leaves, the result would probably have been even more serious.

It is clear, in the third place, that direct and deliberate contact of the foliage and tubers is not necessary for the production of serious

storage rot. This is seen especially by comparing pits 3 and 6 and pits 4 and 7. The corresponding pairs of plots had been dug on the same dates, respectively. The difference consisted in that the foliage had been removed from one each of the two pairs twenty-five days and thirty-three days before digging, while it had not been removed from the other two. This operation brought about two changes in the conditions, either of which might, theoretically, be held accountable for the reduction in the disease. The duration of the blight attack on the foliage was reduced, on the one hand, and with it the supply of spores capable of being washed down to the tubers. On the other hand, the contamination of the soil ceased, and a period elapsed presumably sufficient for the spores present at or near the surface to lose their vitality.

It is not possible to apportion with certainty the exact influence of each of these two factors. This is because the blight, instead of diminishing gradually with the progressive death of the foliage, rallied from the low ebb it had reached about the middle of September (when the first and second diggings were done), and was more severe at the time of the third and fourth diggings. Had it not been so, it was anticipated that there would have been a gradual diminution in the amount of tuber disease found in storage in the series of plots from 1 to 4, and a still more marked diminution in the series 5 to 7. Furthermore, the lifting of plots 4 and 7 had to be hastened owing to the exigencies of farm operations, although it was intended that they should be left until well after the death of the foliage was complete. A reduced amount of tuber disease was again anticipated from this course.

While certainty was not attained, an examination of the evidence shows that the probabilities are in favour of the theory of infection at digging time. In support of this are the following points :—

(1) All the plots went through a very severe blight attack, lasting from the latter part of July until the end of August, with but slight injury to the tubers (as measured by the amount of disease found in them when dug), at a time when they were immature, and theoretically more susceptible to infection.

(2). The amount of blight found in the tubers in the field was slight and, comparatively speaking, uniform ; and it did not vary directly with the date of digging or with the length of the period during which the foliage was allowed to stand. The variations were irregular, though not of great magnitude. The highest total of disease in the field was found in one of the plots dug first, and the next highest in one dug nearly last.

(3) The amount of blight appearing in the tubers in storage, generally speaking, stands in relation to the amount of blight present at and previous to the time of digging.

(4) The general appearance of an increased amount of disease in the crop, which is not visible at the time of harvesting, but becomes so some time afterwards, and which must be due to infection soon before or when the crop is being lifted, can be related to no change in the conditions regularly occurring before digging, but must more probably be referred to the change brought about by that operation itself.

It is not necessary to labour these points. The experiment points generally in the same direction as the series carried out in Canada, and proves that potatoes may become heavily infected with blight when they are brought into contact or close relationship either with diseased stalks or contaminated surface soil. The former possibility will be generally admitted as a danger, as the result of the work of Jensen, Jones and Morse, and the present author. The view that the latter is a serious and hitherto largely unsuspected source of infection is strongly supported by evidence based on laboratory studies of the behaviour of the spores under varying conditions of environment which have been made during the past winter, an account of which will be given in a separate communication.

SUMMARY.

Evidence is presented that more Phytophthora tuber disease may follow a less severe attack of foliage blight, occurring late in the season, than results from a severe outbreak which runs a rapid course.

Conditions favourable to tuber infection may be brought about in Eastern Canada, or elsewhere if the circumstances are similar, if potatoes are sprayed in the early part of the season, but left untreated towards the later portions.

Under such circumstances it is important to distinguish between the disease which appears in the tubers at or very soon after lifting and that which appears some time later. It is the later development of the disease which becomes serious following protracted or late outbreaks of blight.

Evidence derived from field experiments in Canada and in Ireland is presented to show that the bulk of the infection in the case of potatoes which develop blight in storage is contracted when the tubers are being dug.

It is shown that direct contact of the tubers with partially blighted foliage results in serious rot in storage.

The blight does not spread from tuber to tuber even in moist pits to any considerable extent, if at all.

Soil contaminated by means of spores shed from the leaves continues capable of inducing blight in freshly dug tubers which are brought into contact with it over a period of at least ten days, and probably longer.

The part played by contaminated soil is fully established by the results obtained in laboratory investigations, which will be published separately.

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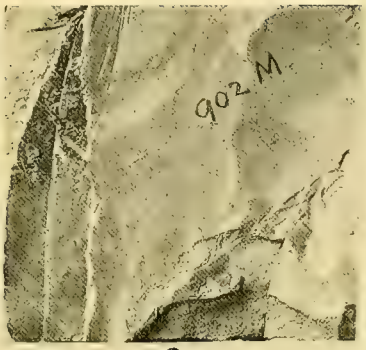

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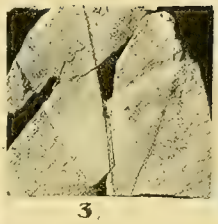

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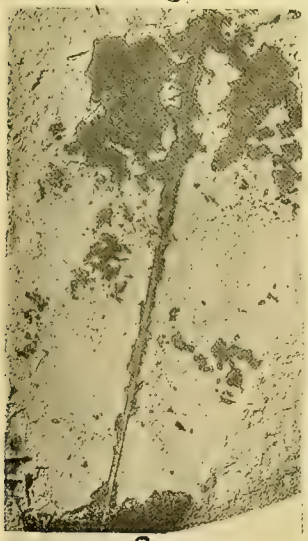

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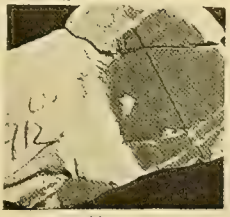

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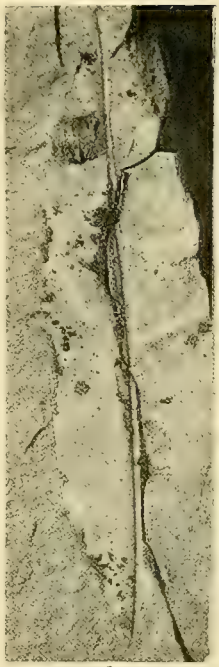

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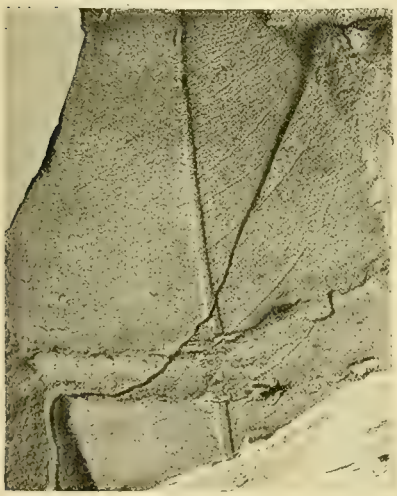

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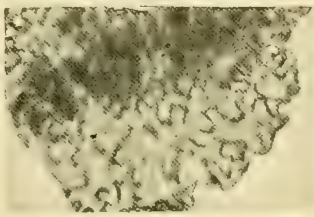

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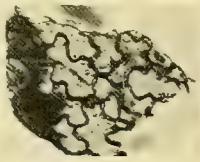

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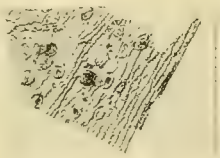

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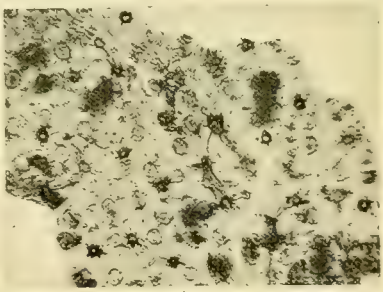

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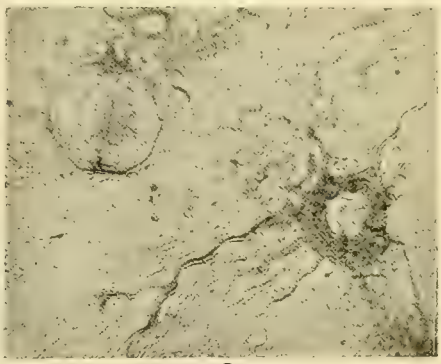

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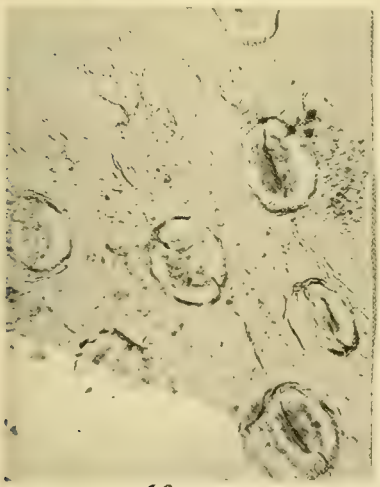

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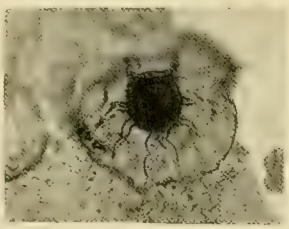

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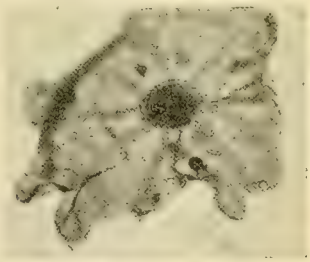

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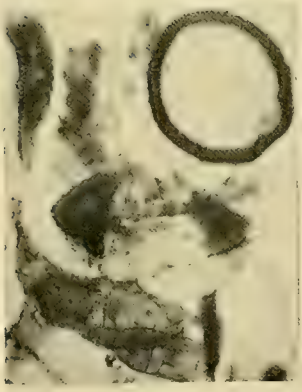

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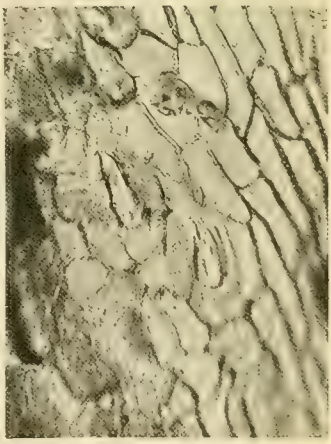

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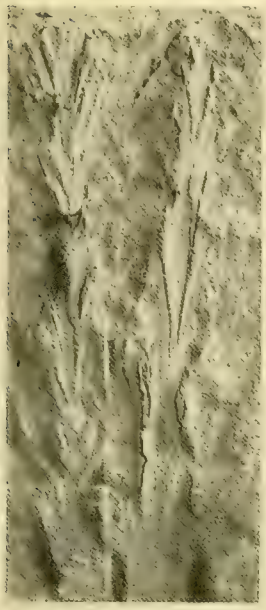

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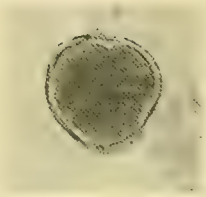

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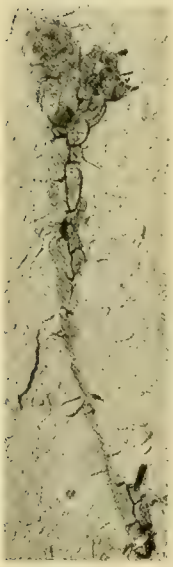

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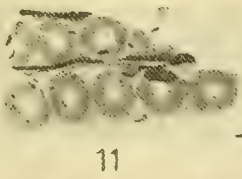

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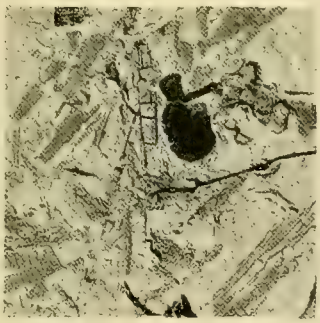

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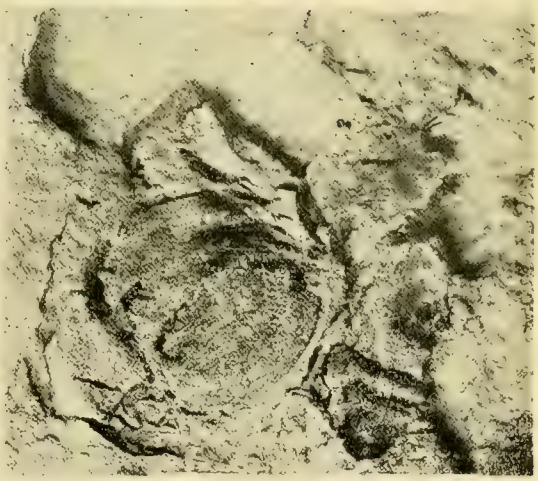

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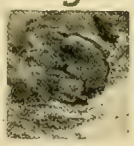

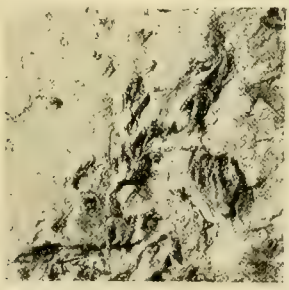

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32.—NOTE ON THE OCCURRENCE OF THE FINGER AND TOE DISEASE OF TURNIPS IN RELATION TO THE HYDROGEN ION CONCENTRATION OF THE SOIL. By W. R. G. Atkins, O.B.E., Sc.D., F.I.C. [Communicated by Professor H. H. Dixon, Sc.D., F.R.S.]

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XXX.

SOME FACTORS AFFECTING THE HYDROGEN ION CONCENTRATION OF THE SOIL AND ITS RELATION TO PLANT DISTRIBUTION.

By W. R. G. ATKINS, O.B.E., Sc.D., F.I.C.

(Communicated by Professor H. H. Dixon, Sc.D., F.R.S.)

[Read November 22, 1921. Published February 2, 1922.]

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Introduction.

It has long been customary to speak of certain soils as acid and of others as alkaline, the terms being used as a rule only when these characteristics were displayed to a marked degree so as to have obvious effects upon the vegetation.

Concerning the nature of soil acidity, a long-standing controversy is still in being, and the views put forward have recently been summarized by

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Fisher (1921). Whether the acidity is produced by humic or other organic acids, by the selective absorption of bases, by the interaction of salts with insoluble alumino-silicates, by the presence of alumino-silicic acids, or by the presence of sulphur acids derived from pyrites, there is only one method of stating precisely the effective acidity—namely, by recording the concentration of hydrogen ions in the soil solution or soil extract. This may be done by giving the hydrogen ion concentration in grams per litre, symbolised as C_H or $[H^+]$, or by using the expression pH, which is defined as the logarithm of the reciprocal of the hydrogen ion concentration expressed in grams per litre. For a discussion of the advantages of this method of stating acidity, reference may be made to Clark (1920). But to render what follows more intelligible to those biologists who are familiar neither with the methods by which hydrogen ion concentrations are determined nor with the terminology adopted, a brief account of the subject is given here.

(a) *Hydrogen ion concentration and acidity.*—The acidity of soils has been measured in various ways, of which an account is given by Clark, but it is found that the behaviour of the soil solution or soil extract towards plants is not correctly shown by titration, which gives a measure of the total replaceable hydrogen, not of the concentration of the hydrogen ion effective at any instant. It is by the latter that the effect on the plant is governed, as well as the effect on enzyme action and the solubility of various salts. For example, equal volumes of N/100 hydrochloric and acetic acids require identical amounts of alkali for their neutralization, but the former solution has a far greater concentration of hydrogen ions than has the latter, since in dilute solution hydrochloric acid is almost completely ionized, whereas acetic is not; it is accordingly said to be a weaker acid. If it is assumed that the ionization of hydrochloric acid is complete at this dilution, its concentration in terms of hydrogen ions is C_H or $[H^+] = 1 \times 10^{-2}$ grams per litre. This may be written

$$[H^+] = \frac{1}{10^2}, \text{ or } pH = \log \frac{1}{[H^+]} = -\log [H^+] = 2.$$

It may at first sight appear to be both cumbersome and unnatural to use such an expressson as pH, viz., $-\log [H^+]$, to denote hydrogen ion concentration, but in practice it is extremely convenient, and gives simple numerical values which are easily remembered. Moreover, since an increase of unity in a pH value denotes a decrease to one-tenth in the hydrogen ion concentration, it is obvious that for any graphical presentation of results difficulties arise when the changes are of the order of 10^{-3} or 10^{-6}, yet these are quite common in researches on this subject. For certain purposes, however, it is at

times convenient to use C_H values. To convert the $-\log [H^+]$ or pH values into C_H or $[H^+]$ values use may be made of semi-logarithmic paper, as pointed out by Roaf (1920). The first decimal points of the pH values are marked off from right to left as abscissae, the C_H values from 0·1 to 1·0 being ordinates against the logarithmic rulings. A diagonal being drawn, the C_H value of any pH value may be read off, the whole number of the latter being the negative power of ten, by which the C_H value so read must be multiplied. Thus, for example, with pH 4·50 it is found that 0·50 on the abscissa corresponds to 0·32 on the ordinate; the C_H value is then $0{\cdot}32 \times 10^{-4}$. Conversion tables are, however, given by Clark, also at shorter intervals by Schmidt and Hoagland (1919). In making a graph for converting pH into C_H values, it should be noted that the logarithmic scale, as on a slide rule, begins at 1, not 0. A further reason for using $-\log [H^+]$ values will be given later on.

(b) *Buffer action.*—If alkali is added to acid, after a certain amount has been run in, a neutral solution is obtained. With a strong acid, such as hydrochloric, the addition of the alkali in successive portions results in a progressive diminution in the hydrogen ion concentration, as may be seen from the fact that the strong acid was largely ionized at the start. But with a weak acid the neutralization of the hydrogen ions existing at any instant results in a new equilibrium being attained by the remaining undissociated molecules of the acid, which become ionized to the same percentage as before. The alteration in the hydrogen ion concentration is therefore much less over a considerable range. If the results are plotted with pH values as ordinates and cubic centimetres of alkali added as abscissae, the slope of the curve will be less steep for the weak acid than for the strong, except near the neutral point. Curves illustrating this are given by Clark (1920) and by Fisher (1921), and in the older literature. A weak acid thus has a considerable "buffer action" in preventing rapid alterations in the pH values, and the same is true of weak bases. Thus peptone and albumen solutions alter in pH value comparatively slowly when acids and alkalis are added. The same is true of many soil suspensions, such as those of peat and calcareous silt; and though these are not solutions, yet they may be considered as having a considerable buffer action, since they yield a continuous supply of a very dilute solution of acid or alkali till exhausted.

(c) *The determination of hydrogen ion concentrations.*—From theoretical considerations Nernst developed an equation connecting the electromotive force of a concentration cell with the concentration of its ions. Platinum black deposited on platinum and immersed in a solution through which pure hydrogen is bubbled constitutes a hydrogen electrode. On the assumption that in very dilute solutions the ions obey the gas laws, it has been shown

that the potential of the hydrogen electrode changes with the concentration of hydrogen ions as follows:—

$$dE = \frac{RT}{nF}\frac{dP}{P},$$

which on integration becomes

$$E = \frac{RT}{nF}\log_e P + A,$$

where A is an integration constant, R the gas constant, T the absolute temperature, n the valency of the ion, and F the faraday or quantity of electricity carried by one gram equivalent of the ion, and $\log_e P$ is the natural logarithm of the partial pressure due to the hydrogen ions. Now, if two such hydrogen electrodes are connected to form a concentration cell, the electromotive force developed is equal to $\frac{RT}{nF}\log_e\frac{C}{C'}$, where C and C' are the concentrations of hydrogen ion, since the ratio of the pressures may be taken as equal to the ratio of the concentrations.

In practice such a hydrogen electrode is connected by an inverted U-tube arrangement, containing a solution of potassium chloride, with a calomel electrode, and the electromotive force of this cell is measured by means of a potentiometer, with all due precautions. The constants being evaluated, use is then made of the following equation to determine the hydrogen ion concentration:—

$$\frac{\text{E.M.F. (obs.)} - \text{E.M.F. (of normal hydrogen and calomel electrode cell)}}{0{\cdot}0001983\ T} = \log\frac{1}{[H^+]} = \text{pH}.$$

Using an N/10 KCl-calomel electrode, this becomes at 25° C.

$$\text{E.M.F. (obs.)} - 0{\cdot}336 = 0{\cdot}9591 \log\frac{1}{[H^+]} = 0{\cdot}0591\ \text{pH}.$$

The fact that the term $\log\frac{1}{[H^+]}$ is thus directly determined is another reason for expressing hydrogen ion concentrations in $-\log[H^+]$ or pH values.

Full proofs of these equations and directions as to the technique may be found in "The Determination of Hydrogen Ions," by Clark.

The method is used as the fundamental one for determining pH values. By its means buffer solutions of accurately reproducible pH values may be standardized for use in colorimetric determinations by means of indicators,

(d) *Neutrality.*—It has not been explained as yet what is meant by a neutral solution or neutrality. Pure water dissociates primarily into hydrogen and hydroxyl ions, and the product of the ionic concentrations is a constant at constant temperature, namely,

$$[H^+] \times [OH^-] = k[H\ O] = K.$$

Since the ions are produced by pure water in equal numbers, the concentration is the same for both when reckoned in gram-equivalents. A solution is accordingly termed neutral when the hydrogen and hydroxyl ions are present in equivalent amounts, as in pure water. With an acid solution the hydrogen ion is in excess, and the hydroxyl is correspondingly reduced, since the product is constant. In alkaline solutions hydroxyl ions preponderate; but as the product is constant, it is possible and convenient to state the reaction of the solution in terms of hydrogen ion concentration rather than in terms of the hydroxyl. One scale, the pH or - log H, is therefore obtained instead of two, based upon the concentrations in pure water, as a starting-point for both.

(e) *The hydrogen ion concentration of pure water.*—It is of interest to determine the hydrogen ion concentration of pure water, but this is attended by many experimental difficulties. Those due to the solution of minute traces of glass may be avoided by the use of silica or platinum vessels, but the absorption of carbon dioxide is still a trouble. It is not possible to determine the pH value by the potentiometer on account of the great internal resistance of the hydrogen electrode half-cell when made up with pure water. The various methods adopted have recently been reviewed by Beans and Oakes (1920). They are as follow:—(1) By deduction from measurements of the electromotive force of concentration cells made up with dilute solutions. (2) By conductivity methods, giving the ionic mobilities of hydrogen and hydroxyl ions in very dilute solutions, which are considered to be valid for pure water; the conductivity of the latter is then measured, and from it and the ionic mobilities the concentration of the ions is calculated. This is the method used by Kohlrausch and Heydweiller (1894), and is the only one of these methods based upon an examination of pure water, but even then use is made of data derived from solutions. For pure water these workers found the hydrogen ion concentration at 26° C. to be $1{\cdot}10 \times 10^{-7}$, or pH 6·96. The value varies with the absolute temperature, as may be seen from the equation given previously. Michaelis (1914) gave for pure water at 16° C., pH 7·10; at 22° C., pH = 7·00; and at 28° C., pH 6·90 (3) By methods based on the hydrolytic dissociation of salts. (4) By

measurements of the rates of certain reactions. (5) By the use of coloured indicators, which give definite tints at known concentrations.

All these methods agree in giving values which are not very far from pH 7·1. Method (5) is used by the writer to test the purity of freshly boiled distilled water and to test glass apparatus for solubility. As shown by its behaviour to brom thymol blue and phenol red, and compared with Clark's standard solutions, the purest, freshly boiled, thrice distilled water which has been prepared here gave pH 7·10–7·05 at about 15° C. Boiling to remove the carbon dioxide in certain types of "hard" glass tube may, however, give any value from about pH 8 upwards, so every tube has to be tested and re-tested after use with alkaline precipitates. If used in the cold, however, such "hard" glass tubes are safe, whereas soft glass tubes are not. Once the indicator has been added the liquid is no longer pure water, hence method (5) is open to objection; but if due precautions are taken in making up the indicator, and if only a very minute amount, say two drops of a 0·02 per cent. solution, is added to 10 c.c. of liquid, the error from this source is slight. Precautions are necessary on account of the fact that pure water has a negligible buffer action.

An entirely new method has been introduced by Beans and Oakes (1920). In this the hydrogen electrode is set up with the purest water, and the cell

$$\mathrm{Hg} \mid \mathrm{HgCl} \,.\, \mathrm{KCl} \mid \mathrm{KCl} \mid \mathrm{H_2O} \mid \mathrm{H_2}$$

is used to charge a condenser of one microfarad capacity, which it does in three to five minutes, whereas a cell of lower internal resistance in which dilute acid is substituted for pure water only requires an instant. Now, the quantity of electricity stored is equal to the product of the E.M.F. of the cell and the capacity of the condenser, viz. $Q = EC$. When discharged through a ballistic galvanometer a deflection d_1 is obtained when the pure water hydrogen electrode is used. Using a standard cell of known voltage a deflection d_2 is shown. Now, since d is proportional to Q, and $Q = EC$, therefore

$$d_1/d_2 = \frac{E_1 C}{E_2 C'} \quad \text{or} \quad E_1/E_2 = d_1/d_2 \,;$$

and, since E_2 is known, E_1 may be found, and the pH value calculated as in the potentiometer method. The value arrived at for pure water at 25° C. is pH 7·91, or $[H^+]$ $1{\cdot}23 \times 10^{-8}$. This differs considerably from the results previously obtained, but the method seems very simple and direct. From the biological standpoint it is not of great importance to ascertain this constant precisely, as pure water is never found in nature, and its reaction is

not necessarily the most favourable for living cells, which can, in different species, tolerate a large range of acidity and alkalinity, a reaction suitable for one being too acid for another.

(f) *The colorimetric method of determining hydrogen ion concentrations.*— In addition to the electrical method, using a potentiometer and hydrogen electrode, or the more recent method with a condenser, which requires a less expensive outfit, the colorimetric method introduced by Friedenthal (1904) and Salm (1904) is available. It is based upon the potentiometer method as a standard, the latter being used to determine the pH values of the buffer solutions, made up to be at convenient intervals on the pH scale. Measured amounts of various indicators are added to these solutions. The electrical method is also used to check sources of error, such as those due to proteins and salts, which cause the indicators to give readings higher or lower than the true values.

The colorimetric method was improved and extensively tested by Sörensen (1909), who introduced new indicators, and eliminated those liable to mislead. More brilliant water-soluble indicators of the sulphone phthalein series were introduced by Clark and Lubbs (1917), as well as standard buffer solutions, having certain advantages over those of Sörensen. The indicators and standard solutions used in this research are those described by Clark and Lubs. A full account of the method is also given by Clark (1920) and by Cole (1920). Clark gives a coloured chart, which can also be purchased separately, and is a great aid to field work and to approximate work in the laboratory. In most cases the colours are faithful renderings of those in the standard tubes, with the same indicator in the specified amount.

It may be added that the preparation of standard buffer solutions by each worker is no longer a necessity, as, owing to the work of Meacham, Hopfield, and Acree (1920), a stable series of salts has been found, which is issued on the market in tabloid form. This series covers the range from pH 2·65 to 9·65 by twenty-eight standards, at convenient, but irregular, intervals. Those in the Clark and Lubs series are uniformly pH 0·2, from pH 1·2 to pH 10·0. In work of this nature care should be taken to check and cross-check the solutions and indicators, both when freshly made up and after storing. It is always advisable to use two or more indicators in orienting experiments, and the use of several indicators greatly increases the accuracy of work carried out without standard tubes.

Methods have also been devised for colorimetric determinations without recourse to standard buffer solutions, by employing, in varying number,

drops of indicators in pairs of test tubes. In one set the full acid tint is developed; in the other the full alkaline tint. On looking through the pairs of tubes intermediate shades are seen. The details are given by Barnett and Chapman (1918), Gillespie (1920), Van Alstine (1920), and Medalia (1920).

(g) *Methods of determining soil reaction.*—Numerous measurements of the hydrogen ion concentration of soil extracts have been carried out by the potentiometer method, notably by Fischer (1914), Sharp and Hoagland (1916), Gillespie (1916), Kappen (1916), Plummer (1918), and many recent workers. To establish the applicability of the colorimetric method to soil investigations, Gillespie (1916) carried out a comparison, using the indicators and standard buffer solutions introduced by Clark and Lubs. He found such a reasonably good agreement as to warrant the general use of the colorimetric method. The agreement holds to within pH 0·2–0·4, but the divergence is usually less. Though the electrical method is regarded as the standard, it is for some solutions open to serious objections owing to chemical changes, such as the reduction of nitrates taking place on the platinum black. Difficulties are encountered also in ensuring that the dissolved gases are not swept out by the hydrogen stream; and though these have been surmounted, both for rapidity and delicacy to a degree well within that required for most biological work, the colorimetric method is to be preferred when based upon carefully prepared standards, which should be checked by the electrical method, if possible, for specially accurate work. The determination of the reaction of the soil has found very numerous applications in agriculture and the related sciences; and since, so far as the author is aware, they have not as yet been utilized in Irish agriculture, a short account will be given of a few of these.

Agricultural application of studies on soil reaction.

The methods have been used, for example, in determining the lime requirements of acid soils by Joffe (1920), Blair and Prince (1920), and by Fisher (1921). Now the soil acidity may in itself be injurious if sufficiently great, or it may simply denote deficiency in alkaline calcium salts, to a shortage of which the evil results may in reality be due, or acidity may lead to the production of poisonous aluminium ions, as will be mentioned later.

Again, the reaction of the medium has a pronounced effect upon the growth of bacteria, protozoa, and fungi.

Gillespie and Hurst (1918) found that when grown in soils of acidity pH 5·2 or more acid, potatoes were rarely affected with scab. Thus those

grown on Caribou loam of pH 4·8 were unaffected, whereas in the less acid Washburn loam much damage resulted. They draw attention to the fact that absolute neutrality is not necessarily the most suitable reaction for a crop. Lipman (1919) has accordingly suggested that the reaction of the soil should be altered to suit the crop, this being effected on the acid side by the addition of sulphur, which is oxidized both by air alone and by bacteria in the soil. This condition is favourable for potatoes. By suitable liming it is then possible to neutralize the soil, thus rendering it fit for the leguminous crops of the rotation, such as clover and alfalfa. This is obviously only possible with certain types of soil.

Working on these lines, Martin (1920) has shown by a most convincing quantitative study how the potato scab, *Actinomyces chromogenus*, Gasperini, may be checked on the Irish Cobbler potato. The soil at the start was at pH 6·03, but treatment with 400 and 600 pounds of sulphur per acre altered the acidities to pH 5·20 and 5·07 respectively, the percentage unsaleable through scab decreasing from 42·9 in the untreated soil to 8·9 and 7·5 respectively in the treated, the total crops being closely the same.

It has, moreover, been shown that there is an intimate relation between the growth of nitrifying organisms and soil reaction. Thus Hesselman (1917–1919) found that both nitrate formation and denitrification are stopped by the acid soil in the mossy type of conifer forest in Sweden. Arrhenius (1920) studied the relation between the pH value of the soil and the organically combined nitrogen, nitrate nitrogen, and nitrogen as ammonium compounds. The maximum for nitrate nitrogen was found at about pH 6·8, after which it decreased rapidly, being reduced to one-sixth at pH 5·5. Nitrogen as ammonia increased sharply from pH 6·3 to 5·8, being nearly twice as great at the latter, but after a flat portion the curve falls, the value at pH 4·8 being identical with that at pH 6·3. Throughout these changes the total nitrogen was much the same.

In direct work on the organism, Gainey (1918) proved the extreme sensitiveness of Azotobacter to slight changes in reaction, pH 6·0 being given as its upper limit. Fred and Davenport (1918) ascertained the critical pH values for the root nodule bacteria of various legumes. For example, the bacteria of alfalfa and sweet clover were unable to stand acidity greater than pH 4·9, whereas those of lupines could withstand up to pH 3·15, other types being ranged intermediately. The alkaline limit appears to be the same for all. Growth is, of course, hindered in the neighbourhood of the limiting concentrations.

Furthermore, the oxidation of various carbohydrates is more rapid in alkaline than in acid solution or suspension. Accordingly, quite apart from

biological decomposition, the accumulation of carbohydrates and similar organic matter is favoured by an acid reaction, and in alkaline soils, such as those of Bihar, India, organic matter may become reduced to such low amounts as to lessen crop production (Davis, 1920).

As mentioned further on, changes in soil reaction induced by manuring may be appropriately studied by the indicator method.

The relation of the ions of the soil solution to its hydrogen ion content.

When studying soil reaction it is well to consider the maximum possible effects produced by the ions present, considered salt by salt. Most attention in this country and the eastern states of U.S.A. has been given to soil acidity, but in some western states, in India, Egypt, South Africa, and elsewhere, alkalinity is the bugbear. The question has been discussed in a recent monograph by Harris (1920). In popular language, "alkali soil" denotes both soil sterile from abundance of neutral salts, which is termed "white alkali," and the truly alkaline "black alkali" soil, in which sodium carbonate is present. The action of the latter on the organic matter gives rise to the black colour. White alkali soil may be reclaimed by irrigation with efficient drainage, whereas black alkali soil is far less tractable, since the alkalinity deflocculates the clay particles.

(a) *Calcium salts.*—Consider now the reaction of water in contact with pure calcium carbonate, such as calcite crystals. This may be taken as the first stage in the production of an alkaline reaction. In the—hypothetical in nature—absence of carbonic acid, the salt has a very slight solubility, which, according to Ruppin (1909), quoting Schloesing, is at 16° C. 0·0131 grams per litre, and has a hydroxyl number of $1{\cdot}05 \times 10^{-5}$, namely, that number of gram equivalents per litre. This corresponds to pH 9·015. Accordingly this limit cannot be surpassed in the more alkaline direction by a solution of pure calcium carbonate In order to test this directly, pure calcite crystals were boiled with water both immediately and after standing for some days. As tested colorimetrically by the method of Clark and Lubs, pH 9·0 was only very slightly surpassed by the saturated solution. With limestone, which may contain small amounts of magnesium, pH 9·2 was reached. The standards are at intervals of pH 0·2, but interpolations may be made. With clear solutions and indicators which show an intensity change only, namely, not a change in tint, or a negligible one, precision can be attained by the use of a Duboscq or Kober colorimeter. The depth of colour varies with the hydrogen ion concentration, but the pH scale is the negative logarithm of this. Over an interval of pH 0·2 it has been found

that the error from this does not exceed pH 0·01, namely, what is judged by intensity or tint to be pHx + 0·10 is in reality pHx + 0·09.

Ruppin has further calculated that a calcium carbonate solution in equilibrium with the carbon dioxide of the air, which exerts a partial pressure of 3×10^{-4} atmosphere, contains five times as much of the carbonate as does a solution in water free from carbonic acid at 16° C. For this the hydroxyl number is 17×10^{-7}, which, being converted, gives pH 8·37. This, then, is the reaction to be expected in a saturated solution freely exposed to the air. In the soil, however, the action of bacteria, protozoa, worms, fungi, and plant roots results in further production of carbon dioxide, so that the equilibrium is displaced in the more acid direction. Bjerrum and Gjaldbaek (1919) have determined by the electrical method that a solution saturated at 18° C. with both calcium bicarbonate and carbonic acid at atmospheric pressure is at pH 5·2. The more carbon dioxide and the more bicarbonate there is in the soil the more acid will be the reaction up to this limit. It is improbable that these conditions are ever realized in nature, nitrogen being present in preponderating amount in the soil atmosphere. The state actually occurring in the soil is not, however, true equilibrium, and carbon dioxide will be given off slowly into the soil air, which is always much richer in this gas than is the atmosphere. The importance of this has of late been emphasized by Howard and Howard (1920) and by Turpin (1920). The value 0·25 per cent. has been given by Keen (1921) as an average for the content of carbon dioxide in the soil air, but Howard has found up to 1·9 per cent. in badly aerated soils in the rainy months at Pusa.

Thus, considering the equilibrium between carbonate, bicarbonate, carbonic acid, and dissolved gaseous carbon dioxide and the disturbance caused by production of the gas in the soil, it is clear that the pH value of the soil solution is dynamic rather than static. This is very evident in soil extracts in which those rich in organic matters rapidly become less alkaline on standing owing to bacterial action. To attempt to measure the pH value of soils to the extremes of accuracy of which the method is capable is, therefore, in most cases waste of time from a biological standpoint, as it will vary with the temperature as affecting the life of organisms, with temperature as affecting the equilibrium quantity of carbon dioxide dissolved, and with the moisture-content as regulating the removal of carbon dioxide from the soil, as well as, indirectly, its production.

Wells (1915) gives the solubility of calcite in contact with the atmosphere as varying from 81 to 70, 61, 52, 44, 38 parts per million as the temperature rises from 0° to 50° C. in 10° steps. From these figures it

follows that as river-water rising in a cold region in contact with limestone flows to a warmer region it must deposit calcium carbonate and become more alkaline in the process, since as temperature rises the carbon dioxide content of the water is reduced, so that the value pH 8·37 at 16° C. is decreased at 0° C. and increased at 35° C. The hydrogen ion concentration of pure water varies, however, in the opposite sense. The water of the River Gandak at Pusa, in Bihar, India, was found to be at about pH 8·6, the air temperature being about 25° C. in November, falling from a much higher value in October. It may be remarked that sea-water is at about pH 8·2 in the Atlantic near the British Isles, but shows seasonal variations, due to photosynthetic action of plankton. The soil in many parts of Bihar, in the basin of the Ganges and its tributaries, is a fine silt, containing 10 to 40 per cent. of calcium carbonate. This soil, with remarkable uniformity, gives pH 9·0, or thereabouts, when freshly shaken up with water free from dissolved salts and carbonic acid. On standing, however, the pH value decreases owing to bacterial action. This deposition of calcium carbonate with the silt appears to stand in relation to the temperature changes undergone by the water in its progress from the cold mountain regions through the plains.

(b) *Magnesium salts.*—In the foregoing, calcium carbonate has been considered as the sole source of alkalinity. Many natural waters, however, contain magnesium carbonate. It has been shown by Moore, Prideaux, and Herdman (1915) and by M'Clendon (1917) that the major portion of the alkalinity of the sea is due to magnesium salts, on account of the greater solubility of magnesium carbonate, about 0·100 grams per litre, as against 0·0131 grams for calcium carbonate. Moore states that sea-water may become more alkaline than pH 9·1 owing to the removal of carbon dioxide by algae. The writer has found that it may even reach pH 9·7, viz., pH 9·95 with thymol phthalein uncorrected for salt error.

Corresponding with the greater solubility, magnesium carbonate, through hydrolysis, gives rise to a greater concentration of hydroxyl ions. Thus with cresol phthalein and thymol blue it was seen that a saturated solution was at least as alkaline as pH 9·6. Using as indicator thymol phthalein an exact match was obtained at pH 10·0, though this indicator is by no means at the end of its range at this point. From this it may be seen that neither soil extract nor natural water can surpass pH 10·0 owing to alkalinity derived from magnesium carbonate. Such a pH value would, however, be fatal to most, if not all, plants. Since calcium carbonate cannot give a value above pH 9·01, it is evident that higher alkalinity is possible where magnesium salts are present with calcium carbonate, as in sea-water.

The relation of these carbonates to marine plants will be discussed elsewhere, but it may be added that the photosynthetic activity of both marine and fresh-water algae or phanerogams is a very efficient process for removing dissolved carbon dioxide and bicarbonates (Angelstein (1911), Nathansohn (1907)), so that a point at or close to the maximum pH value for the carbonate in the solution may be attained provided this does not prove fatal to the assimilating plant. It may, however, be the means whereby one plant destroys another, as has been found to happen with *Ceramium rubrum* in presence of actively assimilating *Ulva lactuca*.

It is not, of course, suggested that a soil containing appreciable amounts of magnesium carbonate is at all as alkaline as pH 10, but this upper limit is higher than that of calcium carbonate. It is possible that the widespread dislike among agriculturists (see Hall, 1910; Russell, 1912; Aston, 1916) towards using limestone rich in magnesium carbonate may have some connexion with this. It has been shown by Hardy (1921) that dolomite retards nitrite and nitrate bacteria, which grow normally with calcium carbonate.

When other salts are present in addition to calcium carbonate the complex mixture may have appreciable effects upon the less soluble constituents. Thus when Merk's pure precipitated calcium sulphate was dissolved in cold water a solution of pH 7·9 was obtained; on boiling to decompose bicarbonate pH 8·3 was found. Thus the traces of carbonate present were insufficient to produce the maximum alkalinity pH 9·0. However, when equal volumes of calcium sulphate solution at pH 7·9 and calcium carbonate (bicarbonate) at pH 7·2 were mixed and boiled, the resulting reaction was over pH 8·8, which suggests a lessening of the solubility of the carbonate through the presence of calcium ions derived from the sulphate. This is conclusively proved to be the correct explanation by boiling water containing both solids in excess. The resulting solution when quickly cooled and tested was at pH 8·0 approximately.

Similarly magnesium sulphate, a good commercial sample, was found to give pH 8·0, rising to pH 8·5 on boiling. Kahlbaum's salt was, however, neutral in solution. On performing a qualitative test with the sulphate and carbonate after boiling pH 9·3 was not surpassed, and with the chloride pH 9·2, the differences doubtless being due to the amounts of sulphate and chloride having been added in small indefinite quantities. Magnesium nitrate was found to give pH 9·6; thus it must have contained an appreciable amount of carbonate. Again, magnesium phosphate in the cold gave pH 8·3, but on boiling this value decreased to pH 7·0, which, after an hour, only altered to pH 6·8; boiling for an extra half hour changed it to pH 6·5. A

sample of calcium phosphate gave in cold saturated solution pH 7·0, which on boiling for an hour and a half reached pH 5·7. From these examples it may be seen that, in making up nutritive solutions for plant-growth to which various nitrates, sulphates, and phosphates are added, a very indefinite reaction may result according to the purity of the salts used. Boiling to sterilize introduces further complications. M'Call and Haag (1920) have shown that nutrient solutions containing acid potassium phosphate have a lower hydrogen ion concentration than similar solutions with the acid phosphates of calcium or magnesium.

(c) *Action of gypsum on alkali lands.*—This type of study is, however, not merely of academic or laboratory importance, but has applications in the reclaiming af alkaline lands. In cases of extreme alkalinity sodium carbonate is present, often in considerable quantity. It is well known that gypsum is beneficial in counteracting the alkalinity. Now, even very minute amounts of sodium carbonate suffice to bring a solution to over pH 10, but by adding gypsum the carbonate is precipitated as calcium carbonate till the equilibrium is obtained for the system in contact with the carbon dioxide of the air. This results in the lowering of the pH value, as may be readily demonstrated. For this purpose a solution of sodium carbonate was made up, and was well over pH 10 as shown with thymol phthalein, which is the most useful indicator for this range, though unfortunately its blue colour is not stable. On adding a little solid calcium sulphate and warming for two to three minutes in a water bath the value fell to pH 8·4. A portion of the same mixture in the cold was at pH 9·4, but had fallen to 8·4 by the next day. Further standing exposed to the air resulted in both heated and unheated mixtures attaining to pH 7·8. Thus this very simple test enables one to study the progress of the action of gypsum or flushing, and to judge the quantities necessary in any given case. A soil which gives any blue with thymol phthalein is probably too alkaline for most crops, as this reagent gives no colour at pH 9·2, but a light blue at 9·4. Thymol blue (thymol sulphone phthalein) gives a blue colour down to about pH 9, and is yellow at pH 8. Cresol red may conveniently be used for the lower range of alkalinity. Soil is certainly fit for crops in India at pH 9·0, or possibly in a somewhat more alkaline state. It is of interest to note that in studying the relation of the calcium content of Kansas soils to the hydrogen ion concentration, Swanson, Latshaw, and Tague (1921) found values up to pH 8·6 for a loamy sand, and pH 8·40–9·03 for Oswego silt loam. These determinations were made by electrometric titration, and the value pH 9·03 is a high value for arable land. The soil originating from limestone in a quarry in Middle Devonian strata near Plymouth, was at pH 9·0 as a maximum. Wherry (1916)

records soil derived from limestone as giving pH 8·5, and that from dolomitic limestone pH 9·0, as determined colorimetrically.

(d) *Solubility of phosphates and occurrence of sulphur acids.*—Another point worthy of consideration is the effect of soil reaction upon the solubility of calcium phosphate. It appears probable that in the presence of calcium carbonate, bicarbonate, and sulphate the influence of the common calcium ion is such as to lessen the solubility of the phosphate. It is well known that the ordinary methods of estimation show low values for "available phosphate" in soils rich in calcium carbonate. Conversely, the action of an acid soil is to increase the available phosphate. Thus in Assam the soils of tea and indigo estates and jungle land have been shown by Davis (1918) to be rich in the latter. Samples, for which the writer is indebted to Mr. W. A. Davis, were found to be as acid as pH 5·4. In this case the acidity was clearly due to the oxidation of sulphur derived from iron pyrites, the latter being found in small grains in ten out of eleven samples; the pyrites had apparently all disintegrated in one surface sample. The possibility of the acidity being derived from organic sources is, it appears, excluded by the fact that the soil samples were not at all of a peaty nature, but of an open sandy texture, some sub-soils being just coarse sand. Furthermore, pyrites alone in water gives an acid reaction pH 4 to 5. Hall (1910) mentions cases where iron pyrites has been the cause of soil sterility, and states that such soils show an acid reaction. Alway (1920, 1), too, mentions a toxic layer of this nature under certain peat lands. Within the last few years much attention has been given to the action of sulphur bacteria in producing acid in the soil. The studies of Gillespie and Hurst and of Martin have already been mentioned in connexion with the control of potato scab. Further, Lipman, M'Lean, and Lint (1916) showed that the biological oxidation of sulphur in the soil produced soluble phosphate. Organic matter favours this, doubtless by providing additional acid and food for the bacteria. Brown and Warner (1917) demonstrated the production of soluble phosphate from rock phosphate by composting with sulphur and manure. Ames and Richmond (1918) and Shedd (1919) studied in addition the effect of nitrification. Tottingham and Hart (1921) found acidity as high as pH 2·9 and 3·1 with sulphur composts, and pH 3·4 and 3·7 with sulphur and rock phosphates. The general relations of inoculated sulphur as a plant-food solvent have been studied by Lipman, Blair, Martin, and Beckwith (1921). It is not, however, only by organisms that sulphur is oxidised. Thus MacIntire, Gray, and Shaw (1921) have shown that in sterile quartz media elemental sulphur is oxidised with production of acid. For its production from iron pyrites they give the following equation:—

$$FeS_2 + 3O_2 \rightleftarrows FeSO_4 + SO_2.$$

From the foregoing it will have been seen that the acidity found in soil is not necessarily due to humus or other organic acids. Of the actual occurrence of acid derived from sulphur, records are not, however, numerous. Beyond those cited by Hall and Alway, the writer has only met with (1) the suggestion by Wherry (1918) that the cause of the acid reaction pH 4·5 of certain spring waters in the United States is the presence of traces of sulphuric acid derived from iron pyrites; (2) the statements of Fischer (1914) and Kappen (1920), both cited from Odén (1921), in relation to the source of acid in humus; (3) the observations of acid water in Utah made by Lee (1907); and (4) the surprisingly great acidity, amounting to 1,360 parts per million of free sulphuric acid, found by Skeats (1902) in Texas. This acidity is slightly greater than N/40, which contains 1,225 parts per million, and corresponds to approximately pH 1·7. Clarke (1916) mentions no further observations; but it is highly probable that were spring waters in regions free from calcareous strata to be tested, the existence of natural acidity due to this acid would be found to be far from uncommon, even in districts remote from known sulphur deposits and the neighbourhood of volcanoes.

(e) *Solubility of iron salts.*—Soil reaction also regulates the solubility of iron salts. The corrosion of iron pipes by moorland water is well known, even though this water may be free from all acids other than atmospheric carbon dioxide, giving a reaction of pH 6·5 only. This appears to suffice to dissolve the metal with formation of ferrous bicarbonate, which is hydrolysed very largely, or almost completely. When, however, water is alkaline, there is much less solution of iron, and this is not without its effect on certain crops. The deficiency of available iron is sometimes considered as a cause of chlorosis, and it may be remarked that at Pusa, *Cajanus indicus*, a leguminous crop, which is much grown, often shows a yellowing of the leaves, the soil reaction being pH 8·7. The soil is a highly calcareous silt, but here the chlorosis may be due to causes other than the small quantity of available iron, for available phosphate is greatly reduced, as shown by Davis (1918). Gile and Carrero (1920) studied the cause of lime-induced chlorosis and the availability of iron in Porto Rico soils with regard to the rice crop. The ash of chlorotic plants was proved to be low in iron. They found that rice became chlorotic in calcareous soils with the ordinary percentage of water, yet would grow normally in certain calcareous soils when the soil was submerged. They state that calcifugous plants become chlorotic on calcareous soils, and advance as an explanation for the behaviour of rice in submerged soil the view that a new kind of root is developed which is better able to assimilate iron, the availability of which is decreased by the alkalinity To the writer, however, it appears that the change in the hydrogen ion

concentration of the soil when submerged may so increase the solubility of the iron salts or oxides present as to give the amount required. For, on imitating the conditions of submergence on a laboratory scale, it was found that the water standing over the soil in a test tube was at first as alkaline as pH 9·0. Even though shut off from external supplies of carbon dioxide, the pH value fell to 7·2 or 7·3 in less than six days, whilst in a day it was down to 8·1 in certain cases; in samples of soil from the top six inches the minimum values were reached more rapidly, as a rule, than in those from greater depths, namely, six to twelve, and twelve to thirty-six inches. In addition to this change in reaction, occasioned by bacteria, which are more numerous near the surface, it must be noted that owing to submergence and the organic matter present the soil is deprived of free oxygen, and so under the reducing conditions iron compounds will tend to pass into the ferrous state, in which they are more readily soluble. It is not, however, to be expected that the reaction of the soil solution itself will change with as great rapidity, or, perhaps, to as great an extent, for the calcium carbonate is continually being attacked by the free carbonic acid, and so a new equilibrium is reached. With excess of carbon dioxide there can, however, be no free carbonate in solution, while there must certainly be free carbonic acid, so the soil reaction must be, at least, no more alkaline than the bicarbonate stage. Bicarbonate gives only a trace of colour with phenol phthalein in boiled distilled water, and this indicator shows a trace of colour at pH 8·0 with Clark and Lubs standards, and a light pink at pH 8·2, the latter being the stage that would ordinarily be observed.

(f) *Effect of manuring upon soil reaction.*—Another point to be considered is the effect of manuring upon soil reaction, in particular with regard to what may be termed the unintentional alterations in reaction. Thus, while lime obviously tends to reduce acidity, and sulphur to increase it, it is not at all so obvious that ammonium sulphate and potassium sulphate should tend to increase it also. Yet the prolonged experiments at Rothamsted, and work elsewhere, have shown this to be so. How far these sulphates have affected the highly calcareous silt of the Pusa manurial series during the fifteen years it has been in existence is a matter for further research. It appears as if the reaction in the plots so treated is about pH 0·2–0·4 less than in other plots (Atkins, 1921); but as bacterial action in liberating carbon dioxide in the soil solution may be more rapid in the presence of these salts, it is uncertain to what extent the results are affected by this. At any rate, the effective pH value—that which prevails in the moist soil in contact with the plant roots—must be lower if bacterial action is more vigorous than in the untreated plots. Sodium nitrate, in which the acid radicle is taken

up, leaving sodium carbonate in the soil, tends to decrease acidity, but the writer has had no opportunity of measuring this effect.

In general, it is found that a garden soil supplied with stable manure in a limestone region in the British Isles gives a reaction of pH 7·0–7·6, though very rich in calcium carbonate, as shown by effervescence with acid. The same soil unmanured varies from pH 8·0 to as much as 9·0 in quarry subsoil. Dressing with seaweed probably tends to give an alkaline reaction on account of the surface contamination with sea salt and salty sand. Another method whereby the alkalinity may be increased or acidity reduced is by burning the surface growth. This well-known device leaves an ash of oxides and carbonates of the plant bases. In one instance examined, the burnt patch of grass in a field gave a good deep pink when tested with cresol phthalein, thus denoting a reaction of about pH·9, whereas the soil around the roots of the unburnt grass was at pH 6·5. The soluble ash alkalis are, of course, washed down by rain, and the bases again become available for plant growth.

(g) *Acid soils.*—So far, with the exception of an account of the existence of free sulphuric acid in soils, soil alkalinity has been discussed; that is to say, the soils with pH values of 7·0 or over. The exact neutral point varies somewhat with temperature, being 7·10 at 16°, 7·00 at 22°, and 6·71 at 40°. Odén (1921) has discussed soil acidity in special relation to the question of the existence of humic acid. He distinguishes between this problem and that of the cause of the acidity actually found, and has shown that preparations of well-washed humic acid give no greater acidity than pH 4·5, owing to the slight solubility of the acid. Since higher acidities may be met with in peat, it is obvious that other acids must be concerned in its production; in the case he gives the acidity of the peat was pH 4·09. Indeed, he quotes various workers to the effect that the extra acidity is due to such acids as sulphuric, phosphoric, acetic, malic, propionic, and others in very minute amounts. Just as calcium carbonate acts as a buffer in alkaline soils, and prevents the reaction being altered to acidity till it is all neutralized, so does humic acid act in acid soils. Odén illustrates this by giving a titration with sodium hydroxide of a peat suspension, noting the pH values after various additions. Unlike the calcium salts got from limestone, which are soluble and are washed out, the humates are relatively insoluble, and remain in the soil as regulators of its reaction.

Thus, to sum up, limestone soils are alkaline, the buffer action depending upon the percentage of carbonate and bicarbonate; peaty soils are acid, the buffer action being proportional to the amount of the humus acids of low solubility. There remain the sandy and clay soils, and these, if free from

carbonate, have less buffer action, especially the sandy. That is to say, percolation with an alkaline water renders them alkaline, with an acid water they become acid; normally they are feebly acid, due to carbonic acid and plant remains. Many are, however, not free from carbonates, and are as alkaline as are limestone soils, though having a lower buffer action. Furthermore, it appears that, owing to adsorption effects, clay soils may have a very considerable buffer action.

The hydrogen ion concentration of heated and unheated soil.

Numerous researches emanating from Rothamsted and elsewhere have shown how profound is the influence of heat in modifying the soil and its extracts, and in effecting changes, both in quantity and character, in the soil population. Recent bacteriology contains many records of the influence the hydrogen ion concentration exerts upon the growth of bacteria, protozoa, and fungi. It is accordingly important to consider how heat may alter the soil reaction.

Grigoriev (1916) noticed that the alkalinity of soil extracts increased during evaporation. Sharp and Hoagland (1919) pointed out that the effect of boiling was very slight or nil in the case of soil extracts lying between pH 5·3–7·3. This has been confirmed by the writer for sandy soil in the region of pH 5·4, which only altered to pH 5·7. But with alkaline soils giving extracts of pH 7·8–8·4 it was found that, on boiling, the carbonate limit, slightly over pH 9·0, was reached through elimination of carbon dioxide. With a soil from Bihar, originally at pH 9·0, when tested by shaking the air-dried silt with boiled distilled water, pH 9·2 was reached, due probably to the presence of traces of magnesium insufficient in quantity to give its maximum carbonate reaction, pH 10·0. Moore (1920) has pointed out that as a rise of pH 1 increases the hydroxyl ten times and diminishes the hydrion by the same factor, the result is a hundred-fold alteration in the relation between amphoteric colloids and their ions. This relation is of the utmost importance in interpreting the effect of changes in hydrogen ion concentration, since these are effective in proportion to their squares. The large alterations in reaction occasioned by heating the extracts of alkaline soils are probably not without a marked effect on the growth of bacteria, etc., subsequently in soil similarly treated. As multiplication progresses, however, the production of carbon dioxide restores the pH value to the neighbourhood of its initial value. How closely this is regained will depend upon how far the soil has been altered physically by heat treatment, which probably leaves it in a rather different state as regards aeration when brought back to its initial water-content. Further research on this subject seems desirable.

Nomenclature of soils with respect to acidity and alkalinity.

Wherry, in dealing with plant distribution in relation to the hydrogen ion concentration of the soil, felt the need of some verbal expression other than quoting pH limits. He accordingly (1919) proposed a convenient terminology which will be used in places in the account of such work which follows, but the pH limits by which they are defined should always be borne in mind. Thus from pH 7–6 is denoted as minimacid, 6–5 as subacid, 5–4 as mediacid, less than pH 4 as superacid. Corresponding terms are used in the alkaline range. This nomenclature is not entirely free from objection, especially on the alkaline side, as there is reason to believe that pH 9·0 up to 9·2, or possibly more, is not as a general rule harmful to plants and certain protozoa, while it is exremely likely that pH 9·7 and over is decidedly injurious to all plant life; yet both are classed as medialkaline, and only at pH 10 is superalkaline reached. Wherry also drew attention to the fact that pH values were not understood by many biologists, and suggested the use of such terms as specific acidity and specific alkalinity, taking the hydrogen and hydroxyl ion concentration of pure water as one. Thus pH 6 is of specific acidity 10, pH 5·5 approximately 30—in reality it is 32—and is given by Wherry as 30 +. Correspondingly on the alkaline side, pH 9 is equivalent to specific alkalinity 100. To the writer these specific values appear to be unnecessary, and to destroy the unity of the one scale, the pH value, which covers all ranges of chemical and biological reaction. Thus, if figures are given, they will be pH values, as is strongly advocated by Clark (1920).

In addition to the terms already given, Wherry embraces the region from pH 6–8 in the term circumneutral. In this limit he places leaf mould, whilst bog peat is from pH 6 to 4 approximately, and "alkali" soil from pH 8 upwards. Upland peat is given as pH 5–7, and limestone soil as 7–9. Fischer (1914), by the electrical method, found for "Hochmoor" sphagnum pH 3·02–3·19, and for "Flachmoor" soil and plant débris pH 5·22–5·95.

A proposal similar to Wherry's was made by Walker and Kay (1912) some years previously for recording the alkalinity (or acidity) of water in terms of specific values, taking pure water at the same temperature as unity. This was made before the use of the pH symbol became general.

Relation of the hydrogen ion concentration of soil to geological formation originating it.

It is obvious that when a soil has been transported so as to lie over strata of different composition from those from which it originated, there can be no relation between the acidity or alkalinity of the soil and rock strata.

From what has been said already it is evident that the supply of bases capable of neutralizing plant remains is the primary factor which regulates soil reaction. In an interesting series of papers, a list of which may be found in the bibliography, from 1916 onwards Wherry studied the relations of the strata to the soil and of the latter to plant distribution. Thus granitic and quartzite rocks have no bases free to act in neutralizing acidity. Slaty rocks are in much the same position, and so are many sandstones. Probably some slates contain a minute amount of carbonate, and sandstones, especially when porous and underlying limestone, may contain notable amounts. The reaction that deeper strata are capable of giving may be indicated by springs, as shown further on.

The following observations may serve to illustrate the relationship. The determinations were made by the colorimetric method, using about a gram of soil to 10 c.c. of water, and testing the approximately clear supernatant liquid. If turbid, the device was adopted of viewing the standards through tubes containing the turbid extract without indicator, the extract of the sample containing indicator being viewed through water to compensate. As explained by Clark, dilution in many cases has not a large effect upon pH, and this was tested with a fine calcareous silt by using only one-fifth the usual quantity of soil and obtaining an indistinguishable colour. The advantage of thus obtaining a clearer solution was obvious. A slight turbidity often increases the buffer action of the solution and lessens errors. With acid soils it appears that larger quantities of solid are necessary to avoid dilution effects. It has sometimes been found convenient to mix the soil with a slight excess of water in a watch-glass, and to test a drop draining away against a white background. As explained by the writer in describing the determination of the acidity of plant tissues, use is made of drops of the standard solutions, or even of the latter rendered turbid by the soil extract. Since the extract has relatively slight buffer action, and that of the standard is intentionally very considerable, the latter is not seriously altered by this; and if identical in pH value with the sample, the error is obviously zero. As a rule, two, or even three, indicators were used in fixing the pH of a sample.

In addition to the indicators given in their final list by Clark and Lubs, it has been found that di-ethyl red—also tested by these workers—is very useful for a region just below that of methyl red. Di-ethyl red changes from yellow to red between pH 6·0 and 5·8, and is increasing in colour just where methyl red is yellow, and where brom cresol purple is turning yellow also. A red colour is very easily observed in a turbid solution, so the value of di-ethyl red in checking the results given by other indicators is

considerable. For the extreme alkaline range, pH 9·4 to 10·0 thymol phthalein is quite the best indicator, though it fades quickly.

In the district round Plymouth, in the counties of Devon and Cornwall, the oldest Devonian formations are on the coast, and the newer are encountered as one proceeds inland in a northerly direction. There are, however, numerous isolated patches of rocks of igneous or plutonic origin.

Thus in Cornwall, near Rame Head, to the west of Plymouth Sound, are found the Dartmouth Slates, in the Lower Devonian. They also extend across to the eastern side. The soil is a dark chocolate brown, and gave the reactions pH 6·7–7·3, as shown in Table I. This siliceous rock yields a soil which may be caused to become acid or alkaline; it appears to have but little buffer action. Some of the results for fields may be due to the addition of limestone as a manure; those parts near the coast—and none are far from it—may be enriched and neutralized by the shells of mussels, periwinkles, and such like brought up by birds, by the use of sea-weed as manure, and by the strong southerly winds carrying minute amounts of sea-spray in suspension. These factors all appear to lessen the production of strongly acid soils near the sea, and they are by no means negligible in their action over prolonged periods. Inland from the Dartmouth Slates come the Staddon Grits, which consist of reddish grits and some slates and shales, with thin limestone bands.

This formation runs east and west on both sides of Plymouth Sound, as shown in the maps of the Geological Survey. The rocks and soil derived therefrom are of a deep red colour, and stand in marked contrast to the Dartmouth Slates, the soil from which is dark brown. In the table may be seen the results given by this formation. It appears to be of definite, but low, alkalinity, except under special conditions, such as where pine needles make up most of the superficial soil, which may be as acid as pH 5·2, and on slate. Apparently these coarse sandstones have become permeated with calcium carbonate from the limestones which originally rested over them. Whatever the cause, the soil is but little less alkaline than that lying directly on limestone, provided it is not practically disintegrated limestone.

The line of separation of the Dartmouth Slates and Staddon Grits lies in the bay containing the Cawsand and Kingsand village. Just to the north of this, on the sound, and for about a quarter of a mile inland, lies a patch of felsite. On this the soil is blackish, and everywhere acid, save in a small glen, bounded on two sides by Staddon Grit, where drainage water and downward movement of soil have resulted in a sufficient admixture of calcium salts to neutralize the acidity. This appears a fertile spot, and is divided up into allotments.

Immediately to the north of the Staddon Grits lie the Mid-Devonian Slates, followed by the Mid-Devonian Limestone. The soil yielded by the limestone varies from near neutrality to an alkalinity of pH 9·0 in quarries and rocky subsoil. Thus it is possible to find soil of about pH 7·6 in both Staddon Grit and the limestone formation. In the Mid-Devonian Slates the soil near the northern limit, viz., next the limestone, is alkaline, pH 8·4; whereas the lower beds give acid soil, pH 6·0–6·8.

Here and there in most of this region there are small patches of Devonian volcanic rocks, which in places are schalstein. This calcareous rock appears to give an alkaline soil also. To the north of the limestone lies a great expanse of Upper Devonian Slate, dotted with volcanic rocks. These slaty rocks yield a soil which, like the Dartmouth Slates may be on either side of neutrality, according to situation and exposure. Thus, whilst there is never enough calcium carbonate to bring the alkalinity up to that of limestone soils, on an average, there appears to be enough, in parts, to prevent the development of any considerable acidity. The Compton district is marked in the map as being schalstein and tuff, hence its greater alkalinity than that of Egg Buckland, where the Upper Devonian Slates are developed. This formation extends northwards for a number of miles, until the metamorphic rocks adjacent to the granite appear. A stream flowing from Compton, below Egg Buckland, is at about pH 8·0, pointing to the existence of calcareous rock, whereas the Dartmoor water is at about pH 6·8.

Northwards again lies Dartmoor, a granite rock covered by peaty soil and siliceous débris. Here, as far as the writer's examination has proceeded, the soil is acid, mostly pH 5·4 to 5·1. It is particularly interesting to note how this acidity extends deep into the subsoil among the débris of the rock. The most acid soil found was that in the crevices of a loosely piled granite wall, which must have been formed almost exclusively of plant remains. This soil at pH 4·1 falls in Wherry's nomenclature into the mediacid group, the general reaction being subacid.

Thus, as one passes inland from the coast to Dartmoor, a very varied succession of soil reactions is encountered. It must not be thought, however, that a district is of uniform reaction; one can only say that it is predominantly of one reaction, as will be seen when considering the relation of the hydrogen ion concentration to plant distribution. For example, Wherry (1920) found that *Sarracenia spp.* abounded in the Dover swamps of Warren County, where the reaction was acid, but in a neighbouring swamp, Green Pond, the water was alkaline, and *Sarracenia*, though common, was only found on hummocks of plant remains, mosses, &c., in which the reaction was acid.

In contradistinction to the acidity developed on granite and felsite stands the alkalinity found in sand dunes and shingle near the sea. Here the

combination of sea-salt, comminuted fragments of shells, and the porous nature of the sand, which permits the removal of bicarbonates, results in a reaction which is always alkaline, often markedly so up to near pH 9·0. To this probably the high temperature reached by sand in the sunlight also contributes, as the bicarbonate may be partly decomposed by this.

It may be added that the Devonian Slate cliffs at Pentire are, in spite of their neighbourhood to the sea, slightly acid, pH 6·6–7·0, whilst the pillow lava or spilite forming the extremity of Pentire Head yields a slightly acid soil, pH 6·8. It is probably due to the wind-borne spray that the acidity is not greater.

It seems possible that within limits the determination of hydrogen ion concentration given by the soil or by the rocks themselves may be of some use in working out relationships of displaced strata where fossil evidence is wanting or scanty. Thus, a slaty or sandy soil may be acid in certain situations, but it is its limit on the alkaline side that may serve to distinguish it.

In this work use has been made of Ussher's (1907) memoir on the Plymouth district.

TABLE I.

Geological formation.	Nature of rock.	Locality.	Soil.	Typical pH values.
Lower Devonian.				
Dartmouth Slates, .	Slaty, . .	Rame Hd. and inland.	Light soil, dark brownish.	6·7–7·3
Staddon Grits, .	Sandstone, . .	Staddon Heights and Maker.	Sandy, deep red,	7·1–7·8
,, ,, .	Slaty, . .	Staddon Heights,	Light soil, brownish.	5·4
Intrusive, .	Felsite, . .	Kingsand, .	Shallow blackish soil, with plant remains.	5·4–6·4
Middle Devonian, .	Slate, . .	Staddon, . .	Light, brownish yellow soil.	6·0–8·4
,, ,, .	Limestone, . .	Plymouth district,	Somewhat sandy, light brown to black.	7·4–9·0
Upper Devonian.				
Volcanic and slates,	Schalstein and slates.	Compton, . .	Brownish soil, light texture.	7·4
Upper Dev. slates, .	Slaty, . .	Egg Buckland, .	Dark brown light soil.	5·8–7·0
,, ,, ,, .	,, . .	Pentire Hd., .	,,	6·6–7·0
Volcanic, .	Pillow lava (spilite),	Pentire Hd., .	Shallow light soil,	6·8
Plutonic, .	Granite, . .	Dartmoor, .	Disintegrating granite.	5·2
,, .	,, . .	Glencullen, Co. Dublin.	Purely peat, .	4·6

The relation of the hydrogen ion concentration of the soil to plant distribution.

Wherry (1916) investigated the distribution of "the walking fern," *Camptosorus rhizophyllus*, in relation to the content of calcium salts in the soil. This was reputed to be a calcicolous species. He was unable to find any correlation, and sought for an explanation in terms of the hydrogen ion concentration. The habitats examined, however, gave a very extended range of values, from pH 5·5–9·0. In his further papers, which are of great interest, he traced the limits for numerous species of native orchids, for the Ericaceae and associated plants, and showed how it comes about that plants typical of the New Jersey Pine Barrens are found bordering a salt marsh. The distribution of species of ferns was also studied by Wherry, who pointed out the bearing that these researches have upon horticultural problems. He thinks it possible to work to an accuracy of pH 0·2, or in the field to pH 0·5. This, however, is considered entirely adequate, for from one plant to another, or even from one root to another, on the same individual observations may differ by pH 1. The writer would, however, point out that Wherry probably means this to hold only over certain ranges of reaction, for in his own experience in acid soils of a particular region great uniformity, to pH 0·2 or less, may be met with. The same is true of the more alkaline soils. But with slightly buffered soils near neutrality varying amounts of carbon dioxide have a relatively large effect.

Some plants appear to have narrow limits of growth, such as certain orchids and heath plants, with which special fungi are associated, as mycorhiza. Again, leguminous plants with root nodules are in their distribution possibly limited by the pH values the bacteria can endure in the soil.

The species studied by Wherry in the U.S.A. are for the most part absent from the British Isles, and the difference in climate may also to some small extent alter the reactions of various situations, so it is of interest to study the problem afresh.

An elaborate contribution to physiological ecology has also been made by Arrhenius (1920), who records not only pH values for different plant associations, but also moisture content, organic matter, calcium, potassium, total nitrogen, nitrate and ammonium nitrogen, and phosphate. The original should be consulted for its valuable details.

In the account which follows, the pH values given for a plant are either from separate districts, or from a quite different soil or situation in the same district. In the field one cannot fail to be impressed with the absence of certain plants from what would appear to be suitable situations; an explanation is often found when the reaction of the soil is examined. As a general

rule the records relate to common and widely spread plants, for it is reasonable to suppose that the absence of these is in any region due to some very definite factor, whereas with the rarer plants it is rather the concurrence of a number of favouring circumstances that renders growth possible. A few of the latter have, however, been mentioned.

With regard to the limitation of the distribution of the weeds of arable land to particular types of soil, a perusal of the lists given by Brenchley (1911, '12, '13) leaves one with the impression that it is hard to draw definite conclusions on the subject, the same plant being met with in very varying soils. Thus, a typical plant of limestone soil may be found in sandy soil, and on examination it has happened that the two soils had closely similar pH values, so far as the writer's experience has gone as yet.

When considering the relation of plant distribution to the hydrogen ion concentration of the soil solution, it is well to avoid the chastisement with scorpions of the modern ecologist by recalling a paper by Foot (1865): "All old floras dogmatically tell us Digitalis avoids the limestone. It is, doubtless, more plentiful on sandstone and clay formation, but grows on limestone also. It is abundant about Mullingar, also occasionally in Burren." The limits given for a species are accordingly only to be taken as embodying the results obtained so far. They do not mean that the species is never found in nature outside these limits; still less do they mean that it cannot grow in water culture outside the limits given. Growth in soil is complicated by many factors. Thus, Hartwell and Pember (1918) have shown that acid soil affects barley and rye differently, and that this is due to the aluminium salts, which do not harm the rye, but injure the barley. The addition of acid phosphate made the soil more acid, but the barley then grew well, as aluminium phosphate was precipitated. Miyake (1916), too, showed how toxic minute traces of aluminium salts were to rice. The effect of the acid is clearly an indirect one in these as in many other cases. This has recently been emphasized by Mirasol (1921), and Comber (1921) instances the different behaviour of a clay soil from that of a peaty soil of equal hydrogen ion concentration. But bearing in mind such very necessary limitations to its application, it is still true that the hydrogen ion concentration may be taken as an index of a set of conditions, physical and chemical, which control plant distribution. Thus, in a soil rich in calcium, the pH value is an index of soil aeration. When this is good the soil will give a reaction close to that for calcium bicarbonate in equilibrium with the air, pH 8·3–8·4, but as aeration becomes less and carbon dioxide accumulates in the soil atmosphere to the extent of 0·25 to one per cent. or over, the pH value decreases. Where there is only a small amount of bicarbonate the soil may even become acid from this cause. The

effects of "sourness" in soil must not therefore be thought of as due merely to the acidity, which may be trifling, and far less than that of the cell-sap of the roots. They are occasioned rather by a series of related causes, such as accumulation of carbonic acid, possibly other acids, and of reducing agents (Gillespie, 1920), deficiency of oxygen, and, in special cases, deficiency in calcium salts and inhibition of the beneficial action of various soil bacteria. What these conditions are for calcareous soils has recently been the subject of a lengthy survey by Salisbury (1920).

From what has been said already, it may be deduced that variations in soil reaction are more likely to be found in sandstone and slate districts than in those where limestone predominates. The buffer action of the carbonate-bicarbonate system prevents wide divergences. The reaction may vary from about pH 8·8–9·0 in a limestone quarry or near the rock to about pH 7·5 in a field, or even less in a well-manured garden. A very average value is in the neighbourhood of pH 8. In sea sand the comminuted shells give a continuous supply of calcium salts long after much of the soluble sodium salts has been washed out. Fisher (1921, 2) has drawn attention to the importance of the buffer action of the soil, and instances the action of basic slag in altering the reaction of a light sand, and not of a heavy loam.

The soils of the province of Bihar, India, illustrate the uniformity of reaction due to calcareous silt. Samples from various portions of the estate of the Agricultural Research Institute, Pusa, were at pH 8·6–9·0, and identical values were given by soils from indigo estates in this province, from different fields in each estate, and at depths of 0–6 in., 6–12 in., and 1–3 ft. Since, in addition to a number of Pusa samples, thirty-six others from three estates were examined, the uniformity of the reaction is evident. Obviously a study of plant distribution in such a district does not extend beyond one type, the calcicolous. A good variety, however, may be obtained in the Youghal district, Co. Cork, and the adjacent portions of Co. Waterford.

A road runs approximately north and south from the seashore through some low-lying sandy country, which is also boggy in parts. To the east on the sea-front is "Clay Castle," a sandy cliff with patches of hard clay; to the west are dunes bordering the rifle range. Further inland are fields under grass, potatoes, turnips, &c., especially along a cross-road to the east. Beyond the latter a glen is entered, with red sandstone quarries; in this the road rises considerably to about 150 or 200 feet above sea-level. Within this limited area, bordering a distance of something over half a mile on the road, the soil reaction varies from pH 8·8 to 5·6, and diverse types of vegetation are found.

Nearest of all plants to the sea one comes across *Salsola Kali.* The sand round its roots gives a solution which is slaty blue with thymol blue, denoting the value pH 9·0. This must be corrected for neutral salt error ; the correction is approximate, and reduces the value to pH 8·8. This extract also gives a good pink purple with cresol phthalein, an indicator which shows no trace of colour below pH 8·2. The reaction is more intense than the sand encrusted by the sea, which was at pH 8·4. On the clayey sand of the face of Clay Castle, *Lotus corniculatus* and *Anthyllis vulneraria* flowered in great profusion, as did also *Erodium cicutarium*, the reaction being pH 8·3.

The sand dune to the west was at about pH 8·4 on the outer side, where were found *Salsola Kali* and *Arenaria peploides,* followed by other plants characteristic of mobile dunes—*Elymus arenarius, Euphorbia Paralias, Eryngium maritimum.* Slightly further in were found *Sedum acre, Convolvulus Soldanella,* and then big patches of *Trifolium repens* and *Lotus corniculatus* at about pH 8·0–7·8, with some *T. pratense* also. To the east the higher ground was grassy, and the sandy soil was evidently capable of but slight buffer action, bare portions among shingle with *Arenaria peploides* giving pH 8·0, and the grassy portions pH 7·2–7·8 with *L. corniculatus, Plantago Coronopus, Taraxacum officinale, Salvia Verbenaca, Ononis arvensis, Erodium cicutarium* L'Hér. var. *hirtum,* etc. Somewhat further inland the higher ground was at pH 8·2, with on the banks *Linaria Cymbalaria, Achillea Millefolium, Galium verum, Bellis perennis,* and further on occasional bushes of *Crataegus Oxyacantha* and *Ulex europaeus.*

Immediately behind Clay Castle the land slopes northwards to a marshy depression. On the slope the soil has more clay mingled with the sand, and no longer gives any effervescence with hydrochloric acid. Its reaction is pH 6·4, as shown by brom thymol blue and brom cresol purple. Here in the dryer portions *Ulex europaeus* is plentiful, and in the wet parts *Iris Pseudacorus, Lychnis flos-cuculi, Orchis sp., Eriophorum sp.* The low portions, where the bog-cotton occurs, merge into a marsh. Here the reaction was found to be pH 7·2, and *Cardamine pratensis* was abundant. It may be mentioned that among the gorse on the higher level were several dumps of rubble and a sandy earth at pH 7·6, the ground around being at pH 6·4. On the dumps were *Bellis perennis, Anagallis arvensis, Sinapis sp.,* and *Malva sylvestris,* none of which were noticed on the acid soil.

The marshy region adjoins the road. On proceeding northwards an embankment facing west was largely covered by *Rubus fruticosus,* abundant grass with a large white clover, *Convolvulus arvensis,* and *Equisetum arvense.* The reaction hereabouts is close to pH 8. The road shortly enters the glen,

but, before following it there, a digression may be made eastwards to study the banks and arable land bordering the cross-road.

Here on the walls facing south the most inhospitable-looking crevices in the mortar are occupied by *Parietaria officinalis,* and give a reaction of about pH 8–8·2. The earth-covered tops of the wall give much the same reaction, and are covered by *Veronica arvensis, Euphorbia Peplus, Taraxacum officinale, Bellis perennis, Senecio vulgaris,* with an odd clump of *Malva sylvestris,* and further on *Capsella Bursa-pastoris* at pH 7·8 or thereabouts. Immediately inside the wall in the grassy ditch were *Convolvulus sepium, Lychnis vespertina,* and *Symphytum officinale.* The reaction both here and in the field was about pH 7·6. The field contained potatoes in part, and was full of weeds, such as *Fumaria officinalis, Euphorbia Helioscopia, E. Peplus, Polygonum aviculare, Papaver Rhoeas, Veronica arvensis, V. agrestis, Scabiosa arvensis, Brassica campestris.*

On proceeding up the glen a by-road to the east is flanked by *R. fruticosus,* with *C. sepium, Urtica dioica,* and some *U. europaeus,* and among the grass *V. arvensis,* the reaction here being close to neutrality, pH 7·2.

Round the stream in the glen the ground is in places marshy, with rushes, *Nasturtium officinale, Polygonum Persicaria, Taraxacum officinale,* the reaction being pH 7·0. The water of the stream, however, was at pH 8·3, close to the value for bicarbonate in equilibrium with the carbon dioxide of the air. Two shallow wells beside it were at pH 6·4 and 6·6, due to excess of carbonic acid, as was shown by insolating the water with filamentous algae growing in it. Photosynthesis then rapidly removed the acid, the alkalinity rising above pH 8 in a few minutes.

The hillside on the east was characterized by the abundance of *Pteris aquilina,* with *Ulex europaeus* and *Rubus fruticosus.* Here the soil was markedly acid, pH 5·6 or 5·4.

On the other side of the road was a ruined cottage and several old red sandstone quarries. Round the cottage the soil was alkaline, about pH 7·8, and supported *R. fruticosus, Convolvulus sepium, Urtica dioica, Symphytum officinale, Anagallis arvensis, Polygonum aviculare, Viola tricolor.* In the quarries the scanty soil in the clefts and ledges was from pH 5·6–6·0. In testing these acid soils without standard solutions use was made of methyl red, di-ethyl red, brom cresol purple, and brom thymol blue. Memory of the tints these indicators give with standards, aided by Clark's coloured chart, enables a considerable degree of precision to be obtained. The clefts and ledges were occupied by *U. europaeus, Cotyledon Umbilicus* (which also grows in among mortar at pH 8), *Silene maritima* With., *Sedum anglicum,* with one clump of *Erica cinerea.* The lower parts with more soil had *Prunus*

spinosa, Veronica arvensis, Fumaria officinalis, and *Achillea Millefolium.* The Veronica and following two plants are usually found on alkaline soil, whereas here it was acid, pH 6·0.

Further examples of lowland acid soil are furnished by the banks of the Blackwater. On the western side the banks slope down steeply to the road. They are wooded, the trees being conifers, oaks, and mountain ash for the most part. Here the soil is peaty and as acid as pH 4·6, grading down to pH 6·4 in the ditch beside the road, a distance of a few feet. The peaty soil is covered with *Erica cinerea* and *Calluna vulgaris.* A certain amount of earth was, however, mixed with it in most parts the reaction being about pH 5·0 with both varieties of heather, *Scilla nutans, Pteris aquilina, Vaccinium Myrtillus,* and on rocky ledges *Polytrichum commune* and *Peltigera canina,* also at pH 5. A drop of four to ten feet brings one to the grassy bank bordering the road. Here are found *R. fruticosus, P. aquilina, Jasione montana, Viola canina, Lonicera Periclymenum,* with stray small plants of *Erica cinerea* and *Calluna vulgaris*; this soil, which is more earthy than peaty, is at pH 5·8. Further along the same bank was at pH 6·4, and supported *U. europaeus, J. montana, Aspidium sp.,* also *Agrimonia Eupatoria,* var. *odorata,* Mill. The absence of heather and bracken may be noted. The drain by the road was also at pH 6·4, and the bare earth was dotted with *Bellis perennis* and a small white clover. On the opposite side of the river the flora was very similar, though the sloping fields were not wooded at the spot examined. The earthy soil was at pH 5·8 on the bank and pH 5·4 in a dry field, from which both *Calluna vulgaris* and *Scilla nutans* were absent.

Upland acid soils may be illustrated by the peat of Glencullen at about 1,200 ft. altitude in Co. Dublin. This peat is at pH 4·6; both *Calluna vulgaris* and *Vaccinium Myrtillus* abound. One sample from Crib Goch, Snowdon, was at pH 5·0, the soil being earthy rather than peaty, and covered with grass, lichens, and also *Lycopodium Selago.* For these two soils the writer is indebted to Mr. L. B. Smyth.

Samples from Dartmoor were found to be very uniformly at pH 5·4–5·1, and were carefully compared against drops of standard buffer solutions on porcelain. Thus, at Staple Tors, both the drier earthy soil supporting *Erica Tetralix* and *Anagallis tenella,* and wetter portions with *Sphagnum sp., Narthecium ossifragum,* and *Drosera rotundifolia,* were at pH 5·4. At Merrivale, about a mile away, an earthy soil with plant remains was grass-covered in the drier parts, and as acid as pH 5·2, the wetter parts with *Eriophorum polystachion* and *Sphagnum sp.,* being at pH 5·4. The most acid soil as yet encountered was obtained from the crevices in a wall of piled granite here. On it grew mosses, a liverwort, and *Jasione montana.* It

turned methyl orange-red, and gave a slaty blue with brom phenol blue, corresponding to pH 4·1. Further on, near Two Bridges, an excavation exposed a granite subsoil. At a depth of three feet this was pinkish in colour, and at pH 5·4, whereas the blackish soil above it at a depth of 4–6 in. was at pH 5·2. In this region were upland pastures, and *Digitalis purpurea* was plentiful. More than a mile up this valley lies Wistman's Wood, a small grove of stunted oaks, gnarled to an extraordinary degree, and covered with lichens. The trees grow between large granite boulders, among which *Vaccinium Myrtillus* and *Sedum anglicum* abound. The soil reaction here was pH 5·1. In the approaches to the wood *Pteris aquilina* is dominant, and the pH value is, doubtless, closely similar, but was not tested.

The flora of sea cliffs was studied mainly at Polzeath and Pentire Head, on the north coast of Cornwall. The coast-line soil is on slaty rock, except at the extremity of the head, where the rock is "pillow lava." In reaction it varies from pH 6·6 to 7·0; the agencies which prevent the development of greater acidity have already been mentioned. The elevation reaches 300 ft. as a maximum, and in the more rocky portions are found *Silene maritima, Armeria vulgaris, Spergularia rupestris, S. rubra, Sedum anglicum.* The sloping banks, on which the grass had been withered by the drought, when seen at a small angle were blue with *Scilla autumnalis*; bushes of *Ulex europaeus* were found on the banks also, together with *Galium verum*, and very small plants of *Plantago Coronopus.* Nearest the sea, and apparently splashed by it at times, were found *Crithmum maritimum*, *A. vulgaris*, and *S. rupestris*, the reaction of the soil in the crevice being pH 8·2. At Youghal the two latter plants were similarly located at pH 7·2–7·6, but spray would at once raise the alkalinity.

In gullies, where streams ran in, the blackish-looking soil was found to be mixed with sea sand, and the boggy parts were at about pH 7·6, prominent plants being *Convolvulus sepium, Mentha aquatica*, and *Epilobium parviflorum.*

Along the coast at Pentire and Polzeath *Sedum anglicum* abounds, but *S. acre* could not be found. As previously mentioned, this region is at pH 6.6–6·8 mostly. Inland, however, about half a mile away, *S. acre* was found on a wall, the reaction being pH 7·8. Since *S. acre* occurs on sand dunes also, and *S. anglicum* on Dartmoor, neither proximity to the sea nor elevation can be considered as limiting factors. One is forced to the conclusion that the hydrogen ion concentration is in this case undoubtedly the factor which determines which of these two species occupies a situation.

Another rather striking instance of such a limitation is shown by *Centranthus ruber*. This has not been observed at less than pH 7·4 on a cliff, but on embankments round limestone quarries it is often the dominant,

if not the only, plant, the reaction being close to pH 9. Near Plymouth an embankment carries a road up to and past Stamford Fort. The south side of this embankment was thickly covered with *C. ruber*. The plant, however, ceased to appear beyond a certain vertical line, save for half a dozen stragglers within ten or twelve feet. Beyond this *Achillea Millefolium* and *Linaria vulgaris* were plentiful, also *Taraxacum officinale*, which occurred in the *Centranthus* area too. On examining the soil, it was found that the latter was at pH 9·0, and on standing with water for a day it only fell to pH 8·8. It had rather more clay-like particles than had the *Achillea* region, the reaction of which was no more than pH 8·2. On standing for a day with water this fell to pH 7·6, showing that the amount of carbon dioxide produced by bacteria was not taken up by excess of carbonate, as in the other sample. Evidently one portion of the embankment was made with limestone rubble from Turnchapel quarries, and the other from a slate near its end, which develops a reaction of pH 8·2 or over, and underlies the Middle Devonian Limestone.

Another point of interest, which, however, requires further work, is the difference in distribution of three species of Convolvulus, all very similar in general habit. *C. Soldanella* occurs on dunes and sand banks where water is not plentiful; aeration is very good, and the pH value 8·0–8·4 denotes the bicarbonate region with but little carbon dioxide. *C. arvensis* occurs in dry situations in fields and on banks, the recorded values being pH 7·6–8·2; these are reinforced by experience of other situations not examined. This range denotes bicarbonate with less efficient aeration and more carbon dioxide. Finally, *C. Sepium* occurs in hedges, in damp thickets, and as a garden weed, the range observed being pH 7·2–7·8. This corresponds with, on the average, rather more carbon dioxide than for *C. arvensis*, namely, with a damper situation.

Certain heath plants are obviously limited in their distribution also; thus *Calluna vulgaris* has been found abundant, at pH 4·6–5·2, on peat or peaty soil. *Erica cinerea*, however, is found in abundance at pH 4·6–5·4; also in drier situations, at pH 5·4, in earthy soil. *Vaccinium Myrtillus* has the distribution of Calluna rather than of Erica. The limits for sparse occurrence are somewhat wider.

Again, *Pteris aquilina* is usually found on acid soil; thus, out of ten situations, six were at pH 5–6, three at pH 6–7, and one at pH 7·6. The latter was certainly a spot rich in Pteris, but it was in a gully below land, at pH 6·4, where the plant was abundant.

In this description, and in the table which follows, dominant means plentiful to the more or less total exclusion of other plants; abundant means

that numerous patches or groups of the plant occur; and plentiful that numerous isolated plants are found.

Ulex europaeus is widely distributed, but its occurrence is mainly in the acid region. Thus, out of twenty-seven situations, five were from pH 5·4 to under pH 6, sixteen were from pH 6–7, two pH 7–8, and four pH 8–8·6. Of those beyond pH 7, only one at pH 7·2 was an abundant situation, and two were single bushes only. The remaining three were situations with a number of isolated bushes. It is plentiful on soil above limestone around Cork Harbour, but no opportunity of examining these regions has arisen. It is possible that the soil is boulder clay not derived from the limestone.

Rubus fruticosus must be placed among plants with a wide range, having been found between pH 5·4 and 8·4, being distributed abundantly through the whole of it. However, Briggs (1880) records thirty-eight sub-species in his Flora of Plymouth, and twenty-two are recognized by Hooker (3rd ed., 1884), not including *R. saxatilis*, which is given as a species. It is probable that a study of the varieties would show a less extended range.

The foregoing outline may be amplified by reference to the alphabetical list of plants in Table II, which records the pH limits. It is hoped that both species and situations may in the future be examined in greater number.

So far no reference has been made to the reaction of the soil carrying crops, since their occurrence is directed, and not natural. It is, however, a subject of much importance. One can instance the work already mentioned on the occurrence of potato scab; a paper accompanying this points out a relation with the "finger and toe" disease of turnips and other Cruciferae. It will be of interest to see whether many of this group are unable to thrive in soil even slightly acid; the majority are recorded by Briggs as occurring in localities known to the writer to have predominantly alkaline reactions, many exclusively so. If an alkaline region is acid in any part, this is either a boggy spot or a steep bank from which bicarbonate is readily leached out. Since it is laborious and costly to alter the reaction of the soil to suit the crop, the alternative is to choose the crop to suit the soil reaction, and this is being done to a considerable extent in Sweden, Germany, Austria, and the United States, where, in Minnesota, for example, as described by Alway (1920, 1 & 2), peaty soils are being brought into cultivation by supplying their deficiency in phosphates and sometimes in potassium, the crops most commonly grown being grasses for hay, onions, celery, lettuce, potatoes, beets, etc. The subject is undoubtedly worthy of greater attention in Ireland, as such large areas of peaty land occur. As mentioned previously, an acid peaty soil differs in important respects from a clay soil of equal hydrogen ion content.

It may be added that in Bihar *Indigofera arrecta* grows before the first cutting to about four feet. The reaction is about pH 8·7 or over, and available phosphates are low in many places in the calcareous silt. In parts of Assam, when grown on certain tea gardens with an open sandy soil and an abundance of available phosphate, the indigo grows luxuriantly, reaching ten feet before the first cutting, and twelve to fifteen in a year. The soil reaction is about pH 5·4–6·2, which favours the liberation of phosphate. It is of importance to note that the sub-soil was very well aerated, being a coarse sand in some cases. This means that iron salts must have existed largely in the ferric condition, and that toxic aluminium salts must have been absent or only present in minute amounts. With an equally acid clay soil their concentration would probably have been greater.

TABLE II.

Plant.	Situations observed.	Limits of occurrence, pH.	Notes.
Achillea Millefolium, . .	8	6·0–9·0	Mainly over pH 8.
Agrimonia Eupatoria, . .	2	6·8–8·2	
A. Eupatoria, var. *odorata* Mill,	2	5·4–6·4	
Alliaria officinalis, . .	2	7·0–7·4	
Alyssum maritimum, . .	2	7·6–8·2	Abundant where found.
Anagallis arvensis, . . .	7	7·2–8·2	
A. tenella, ...	1	5·4	Abundant.
Anthyllis vulneraria, . .	1	8·3	Do.
Arabis hirsuta, . . .	1	8·6–9·0	Scarce.
Arctium Lappa, . . .	1	5·4	
Arenaria peploides, . . .	2	8·0	Plentiful on sand and among shingle.
Armeria vulgaris, . .	3	6·6–8·2	Abundant at pH 6·6.
Bellis perennis, . . .	7	5·4–8·4	Abundant about pH 8.
Brassica campestris, . . .	1	7·6	
B. Sinapis, Vis., . . .	2	7·6–7·8	
Calluna vulgaris, . . .	6	4·6–5·8	Abundant at pH 4·6–5·2.
Capsella Bursa-pastoris, . .	4	6·8–7·8	
Cardamine pratensis, . .	4	6·8–7·6	Plentiful at pH 7·2.
Centranthus ruber, ...	6	7·4–9·0	Abundant at pH 8·6–9·0.
Chrysanthemum Leucanthemum,	5	6·6–8·2	
Circaea luteliana, . . .	1	7·2	
Cochlearia danica, . . .	4	7·6–7·8	Plentiful.
Convolvulus arvensis, . .	4	7·6–8·2	
C. sepium, ...	6	7·2–7·8	
C. Soldanella, ...	1	8·0	On dune sand.
Cotyledon Umbilicus, . .	8	5·4–7·8	Acid rocky banks and mortar of walls.
Crataegus Oxyacantha, . .	8	5·4–8·0	Only surface soil examined.
Crithmum maritimum, . .	3	7·5–8·2	Plentiful.
Digitalis purpurea. . .	2	5·4–7·2	Plentiful at pH 5·4, earthy soil.

TABLE II—*continued.*

Plant.	Situations observed.	Limits of occurrence, pH.	Notes.
Drosera rotundifolia, . .	1	5·4	Plentiful.
Elymus arenarius, . .	1	8·0	Abundant on sand.
Epilobium parviflorum, . .	1	7·6	Plentiful.
Equisetum arvense, . .	1	8·0	
Erica cinerea, . . .	6	4·6–6·0	Abundant pH 4·6–5·4, peaty soil or earthy.
E. Tetralix, . . .	1	5·4	Abundant.
E. vagans, ...	1	6·2	In cultivation with *E. cinerea*.
Eriophorum polystachion, . .	1	5·4	Plentiful pH 5·4, soil rather peaty.
Eriophorum sp., . . .	1	6·8	Possibly one species.
Erodium cicutarium, var. *hirtum* L'Hér.,	2	7·4–8·3	Plentiful.
E. moschatum, L. Hér., . .	1	8·0	
Euphorbia Helioscopia, .	2	7·0–9·0	Plentiful pH 8·6–9·0.
E. Paralias, . . .	2	8·0–8·2	Plentiful on dunes.
E. Peplus, ...	2	7·0–7·6	Plentiful in field.
E. portlandica (E. segetalis), .	1	8·2	On sandy waste.
Foeniculum vulgare, . . .	1	8·6–9·0	
Fumaria officinalis, . . .	2	6·0–7·6	
Galium verum, . . .	3	7·4–8·0	Plentiful.
Hypericum Androsaemum, . .	1	6·8	
Iris foetidissima, . .	1	6·2	Dry soil. Frequent on limestone soils, viz. pH 8.
I. Pseudacorus, . . .	1	6·4	Plentiful in wet soil.
Jasione montana, . . .	6	4·1–6·8	
Linaria Cymbalaria, . .	7	6·6–8·0	Plentiful, banks and in mortar.
L. vulgaris, ...	1	8·2	
Lonicera Periclymenum, . .	3	5·8–6·2	
Lotus corniculatus, . .	6	7·2–8·4	Plentiful.
Lychnis diurna Sib., . .	7	6·1–7·4	
L. Flos-cuculi, . . .	1	6·4	
L. vespertina Sib., . . .	1	7·6	
Lycopodium Selago, . . .	1	5·0	Earthy soil, Snowdon.

TABLE II—*continued.*

Plant.	Situations observed.	Limits of occurrence, pH.	Notes.
Malva sylvestris, . . .	3	7·6–8·4	
Mentha aquatica, . . .	1	7·6	Plentiful.
Narthecium ossifragum, . .	1	5·4	Plentiful, somewhat peaty soil.
Nasturtium officinale, . .	1	7·0	
Nepeta Glechoma, . . .	3	6·0–7·4	
Ononis arvensis, . . .	3	7·5–8·2	
Orchis sp., ...	1	6·4	
Papaver Rhoeas, . . .	1	7·6	
Parietaria officinalis, . .	2	7·6–8·2	Plentiful in mortar.
Peltigera canina, . . .	7	5·0–7·6	Plentiful even at the extremes.
Plantago Coronopus, . . .	7	7·0–8·4	
Polygonum aviculare, . .	2	7·6–7·8	
P. Persicaria, . . .	1	7·0	
Polytrichum commune, . .	1	5·0	Peaty soil.
Poterium Sanguisorba, . .	4	6·2–8·0	
Primula veris, . . .	3	6·7–7·4	
Prunella vulgaris, . . .	3	5·6–7·0	
Prunus spinosa, . . .	3	5·4–6·2	Earthy soil; surface only tested.
Psamma arenaria, Beau., . .	1	8·2	Abundant on dune.
Pteris aquilina, . . .	10	5·0–7·6	Abundant pH 5·4. Limit 5·0–6·4 save for one at 7·6, which, however, was an abundant occurrence.
Rhododendron sp., . . .	1	5·4	Surface soil only tested, but neighbourhood all acid.
Rubia peregrina, . . .	2	6·2	Plentiful.
Rubus fruticosus, . . .	17	5·4–8·4	Tendency to group around pH 6 and 8.
Salsola Kali, . . .	2	8·0–8·8	
Salvia Verbenaca, . . .	6	7·0–7·7	Abundant around pH 7·6.
Scabiosa arvensis, . . .	1	7·6	
Scilla nutans, Sm., . . .	4	5·0–7·6	Abundant around pH 5.
S. autumnalis, . . .	2	6·6–7·0	Abundant.

TABLE II—*continued.*

Plant.	Situations observed.	Limits of occurrence, pH.	Notes.
Sedum acre,	5	7·0–8·0	Abundant.
S. anglicum,	4	5·4–6·0	Abundant.
Senecio vulgaris,	5	7·6–8·4	
Silene maritima, With.,	7	6·0–7·8	Abundant at pH 6·6–6·8.
Spergularia rupestris,	3	6·8–8·2	Plentiful at pH 6·8.
S. rubra,	1	6·8	
Sphagnum sp.,	1	5·4	Abundant.
Stellaria Holostea,	3	6·7–7·3	
Symphytum officinale,	2	7·6–7·8	
Taraxacum officinale,	9	6·1–9·0	
Trifolium pratense,	2	7·8–9·0	
T. repens,	2	8·0–9·0	
Ulex europaeus,	27	5·4–8·6	Abundant at pH 6·0–6·8.
Urtica dioica,	5	5·4–7·8	Abundant about pH 7·8.
Vaccinium Myrtillus,	3	4·6–5·1	Plentiful.
Verbascum Thapsus,	3	7·6–9·0	Single plants.
Veronica agrestis,	1	7·6	
V. arvensis,	5	6·0–8·4	Plentiful about pH 8.
V. Chamaedrys,	4	6·0–7·4	
Viola canina,	5	5·4–6·7	
V. tricolor,	1	7·8	

Garden cultivation of wild plants.

It is well known that certain of our native plants die out in gardens unless in soil similar to that in which they occur naturally. The writer is indebted to Mrs. E. W. Sexton for information regarding attempts to grow the following in ground behind the Marine Biological Laboratory at Plymouth. The soil is over limestone, and varies in reaction from about pH 7·6–8·2.

It was found that when transplanted the plants always died in the case of *Anagallis tenella*, *Calluna vulgaris*, *Drosera rotundifolia*, *Erica cinerea*, *Narthecium ossifragum*, *Scilla autumnalis*, *Sedum anglicum*, and *Vaccinium Myrtillus*. Elsewhere *E. cinerea* and *E. vagans* grew well in a garden at pH 6·2.

Among those which flourished were *Anthyllis vulneraria*, *Armeria vulgaris*, and *Sedum acre*. Reference to Table II shows that the pH value of the soil is correct for the latter, but incorrect for the former list.

Sedum album also flourished, but has not been found growing wild. This is sometimes called *S. anglicum* by florists, which serves to explain a puzzling instance in which *S. anglicum* was alleged to grow well in limestone gardens near Plymouth and Cork. The two were evidently confused, as the species of this genus often are (Praeger, 1921). It is stated in the Cybele Hibernica that *S. album* grows wild in several places near Cork. Due attention to the correct soil reaction will render the growth of wild flowers less precarious in captivity. Wherry (1918) has pointed out that, though most orchids require an acid soil, yet certain species, of Cypripedium for example, have slightly alkaline habitats.

The hydrogen ion concentration of natural waters in relation to plant distribution.

When considering the reaction of the soil it is natural to inquire into that of the water draining or springing from it, and the relation it bears to plant distribution. Mention has already been made of the existence of certain springs which contain sulphuric acid. These, however, are rather rare.

Birge and Juday (1911) made a detailed examination of the Wisconsin lakes, correlating the animal and vegetable life with the alkalinity of the water to phenol phthalein, or its acidity to the same indicator. This monograph studies the oxygen content of the water also, and is a mine of information. Chambers (1912), too, observed the seasonal changes in the alkalinity and oxygen content of the ponds in the Missouri Botanic Gardens according as the algae abstracted carbonic acid and evolved oxygen. The numerous researches on the hydrogen ion concentration of sea water and its relation to the photosynthetic activity of the algal plankton will be discussed elsewhere.

More recently Saunders (1921) has shown that the water from wells and of the town supply at Cambridge is very constantly at pH 7·1–7·2, the districts examined being chalk and gault. Running streams, however, lose carbon dioxide till the bicarbonate equilibrium with the gases of the air is

reached, values of 8·25–8·5 being obtained for them, and for clean large ponds. Attention was also drawn by Saunders to the effect of photosynthesis in raising the reaction of the water to as much as pH 9·0 in a small pond containing masses of *Spirogyra.*

The writer has examined a variety of natural waters, the reactions of which are tabulated below.

TABLE III.

Source.	Locality.	pH.	Notes.
R. Gandak, . .	Pusa, Bihar, . .	8·6	Approximate value from colour chart with cresol red and thymol blue. The soil around is at pH 8·6–9·0.
Tap, . . .	,, ,, . .	8·0–8·2	Purified river water.
,, . . .	Basingstoke, Hants, .	7·2	Deep well supply, hard water, chalky district.
,, . . .	Lowestoft, Suffolk, .	7·8	Approximate. Hard water. Gave pH 9·1 when boiled.
,, . . .	London, . . .	8·0	Approximate. Hard water.
Reservoir, . . .	Blagdon (Bristol), . .	7·8	
Tap, . . .	Cork, . . .	6·9	R. Lee water, filtered.
,, . . .	Youghal, Co. Cork, .	7·0	
,, . .	Plymouth, Devon, . .	6·8–7·0	Dartmoor water; soil about pH 5·4.
Rain, . . .	,, ,, .	5·9	Collected in copper rain-gauge between 3 p.m. and 9 p.m., after a wet morning in November. Air was accordingly dustless. Examined an hour after collecting. Soon rose to pH 6·2 and over owing to solution of glass.
Stream, . . .	Brixton, Devon, . .	8·2	
,, . . .	Compton, Devon, . .	8·0	Schalstein and Devonian slates area, gave pH 8·96 when boiled.
,, . . .	Youghal, Co. Cork, .	8·3	Soil around at pH 7·0; earthy soil on hillside pH 5·4.
Shallow wells, . .	,, ,, .	6·4–6·6	Partly supplying the stream. Insolation with algae raised this water to the neighbourhood of pH 9.
Shallow well, . .	Maker, Cornwall, . .	6·7	The Staddon grit-soil around is at pH 7–7·8.
Small reservoir, . .	Staddon Heights, Devon,	8·0	Or somewhat more. May.
,, ,, . .	,, ,, ,,	8·4	In full sunlight, October. The water was green, with green flagellates, abundant *Tetraëdron minimum* and *Scenedesmus obliquus*; when insolated in a bottle it rose to pH 9·7, denoting presence of magnesium salts.

TABLE III—*continued.*

Source.	Locality.	pH.	Notes.
Pipe from well supplying the reservoir,	Staddon Heights, Devon,	6·8	
Large pond, inlet, .	Blachford, Cornwood, Devon,	7·02	R. Yealm flows in and out of this pond; Dartmoor water; May.
Large pond, among weeds.	,, ,, ,, .	7·37	
Large pond, outlet, .	,, ,, ,, .	6·93	
Pond water, . .	,, ,, ,, .	6·80	In October. Gives pH 8·5 on boiling.
,, ,, . . .	,, ,, ,, .	6·40	In November. *Myriophyllum spicatum* grows here.
R. Yealm, . . .	,, ,, ,, .	6·58	November, at rapids below pond. Note increase in pH by aeration.
Leat, . . .	,, ,, ,, .	6·41	Leat water comes from Yealm, just above rapids. It supplies tank.
Trout tank, . .	,, ,, ,, .	6·42	
Small stream from pipe,	,, ,, ,, .	7·3	Flows into pond from west. On boiling, it reaches pH 8·9, and is therefore much richer in calcium carbonate than the river water.
Garden pond, . .	,, ,, ,, .	6·3	*Lemna minor* in abundance.
Small stream, . .	,, ,, ,, .	6·7	Flows into Yealm from east, above pond.
Small stream from pipe,	,, ,, ,, .	6·4	Flows into Yealm from east, below pond.
R. Piall, . . .	Slade, Cornwood, . .	6·83	In late October; flows into Yealm from west.
Spring, . . .	,, ,, . .	6·0	From pipe. Siliceous rocks of Culm measures; October.
,, . . .	,, ,, . .	6·7	From pipe. Different origin.
Small tank, . .	,, ,, . .	7·1	Supplied by second spring. In among weeds.
Loch Lannsaidh, .	Dornoch, Scotland, .	7·1	Gave pH 8·8 when boiled. November sample; poor in plankton; had *Gymnodinium sp.* (colourless Peridinian), common; green flagellate; a few diatoms *Asterionella sp.* and *Nitzschia sp.*; also a small, round green alga.

It should be noted that the Dartmoor drainage water of the R. Yealm is at a lower pH value in November than in May or October. This is probably due to the fact that in a rainy month it more nearly approximates to rain-water, and contains less calcium bicarbonate. The decay of leaves and the

less vigorous photosynthesis of the diminished plankton and water plants also tend to increase the amount of carbon dioxide; and, furthermore, the lower temperature of the water results in a large amount being retained in solution. These factors also tend to diminish the pH values, namely, to increase the hydrogen ion concentration.

From what has been said already it will at once be recognized that these results recorded in Table III point to the effect of the carbon dioxide from the air and from the soil gases in lowering the reaction that could be produced by the amount of calcium carbonate present. Even with upland water from Dartmoor taken from the R. Yealm at Blachford the acidity pH 6·8 is entirely due to excess of carbonic acid. On driving this off, by boiling in a carefully tested hard glass tube, as a maximum value pH 8·5 was reached. Assuming this to be due to calcium carbonate (viz., not to magnesium), it is possible to calculate the concentration of this salt. A saturated solution contains 0·0131 gram per litre, and gives as reaction pH 9·015 or C_{OH} $1{\cdot}05 \times 10^{-5}$. Now, pH 8·5 corresponds to C_{OH} $3{\cdot}2 \times 10^{-6}$; and therefore to 0·0040 gram per litre if it be assumed that at these dilutions the concentrations of the hydroxyl ions are proportional to the amounts of calcium carbonate.

The assumption may not be quite correct; for a more concentrated solution it certainly would be erroneous (see Clark, 1920, p. 29). To test this directly, a solution was prepared by boiling distilled water with calcite. In reality, the solution was not quite saturated, as it gave pH 8·96 instead of pH 9·01. This was diluted with the same distilled water, which when freshly boiled was at pH 7·1, as shown by brom thymol blue and phenol red, two volumes being added to one of calcite solution. When freshly boiled, this mixture was at pH 8·6 to both cresol red and thymol blue. Since it contains 0·004 gram per litre, the calculation showing that the solution at pH 8·5 contained 0·0040 gram must be tolerably correct. This method for finding the bicarbonate content of such soft waters is very rapid; its use will be treated in more detail elsewhere. The solution at pH 8·5 is of normality 4×10^{-5} with respect to calcium carbonate. This is just over three-tenths of the amount required for saturation in absence of carbon dioxide, but only about six per cent. of saturation when in equilibrium with the atmosphere. Photosynthesis in Blachford water cannot therefore produce a reaction more alkaline than pH 8·5 as an upper limit. This was tested with a small glass aquarium which had stood nearly four months with Blachford water and the plants growing naturally in it. In subdued light the tank was at pH 6·8. After an hour and a quarter in full October sunshine it had risen to pH 7·6, and after three and a half hours to pH 8·6. This is slightly above the limit reached by boiling the Blachford water direct, but the prolonged exposure

to the glass probably brought traces of alkali into solution. A duplicate with half Plymouth tap-water and half Blachford water also reached pH 8·6. A third vessel in good north light, and plentifully supplied with algae in Blachford water, was at pH 8·5; and a fourth which had stood for over a year, with added chalk, was at pH 8·95 when similarly illuminated. Since pure calcite, when boiled with water, only gives a reaction slightly over pH 9·0, this is near the limit. The value pH 9·7 given by the Staddon reservoir water, with its natural algal flora, is probably explicable on the assumption that small amounts of magnesium were also present, as is highly probable in a situation a quarter of a mile from the sea. Similar high values are found in sea-water during insolation with algae. Such photosynthetic changes have been studied in relation to their dynamics by Osterhout and Haas (1918).

Thus, both under its natural conditions and during intense insolation in jars, soft upland water, such as the Blachford and Plymouth water, is less alkaline than a water richer in the carbonates of the alkaline earths. The difference in the algal and general flora is probably correspondingly marked, though as yet it has not been examined in any detail. It is well known, however, that certain species are found mainly or exclusively in these soft waters, and the correlation of their occurrence and the pH value of the water will be of interest. Skene (1915) showed a striking relationship between the occurrence of various species of Sphagnum and their powers of growth in solutions of different normality, from N/250 to N/5000 acid or alkali. A study of the water in which they occur would probably demonstrate that the hydrogen ion concentration is of importance here also.

With natural waters of low bicarbonate content the buffer action is extremely slight, so great care must be taken in the preparation of the indicators, of which small quantities only should be used, so as to minimize error from the reaction of the latter. With solutions which are boiled the indicator should be added only after cooling again. Whenever possible, the use of two indicators is recommended, one with the middle region of its range above and one below the reaction of the liquid being tested. Rubber stoppers should also be kept away from water samples, since in contact with distilled water a reaction of pH 5·4 may be developed. Prolonged boiling of the rubber with changes of water minimizes this error. Special care should be taken to avoid contact with the ground-glass portion of stoppered bottles, especially those of white glass. Distilled water may become sensibly alkaline in a bottle; accordingly every bottle used should be tested.

Pure toluene has been found serviceable in preventing the growth of moulds in the Clark and Lubs standard buffer mixtures.

In conclusion, it must be stated that the experimental work recorded in this and the accompanying papers was carried out in the School of Botany, Trinity College, Dublin, and at the Marine Biological Laboratory, Plymouth. Determinations were also made at the Agricultural Research Institute, Pusa, India, and at various other places during field work. To the Directors of the laboratories mentioned the author wishes to record his indebtedness for the facilities afforded. The work was rendered possible by a grant from the Department of Scientific and Industrial Research, which covered the expenses of the special reagents. Thanks are also due to Mr. W. A. Davis, Pusa, for numerous samples of soil; to Dr. E. L. Fox, Plymouth, and Mr. C. A. Pode, Slade, for water samples and access to streams; also to Miss M. V. Lebour for some plankton identifications.

The bibliography is common to the three papers issued in this cover, and, with but few exceptions, references to be found in Clark's (1920) list have been omitted from it. They may be identified there by name and date given in the text.

Summary.

1. The theoretical maximum alkalinity due to calcium carbonate only is pH 9·01, which may be attained experimentally in the absence of carbon dioxide. The corresponding bicarbonate in equilibrium with the gases of the atmosphere is at pH 8·37 at 16° C., becoming more alkaline at higher temperatures. Owing to the high content of carbon dioxide in the soil, the pH values of limestone soils are usually lower, and vary with the aeration.

2. The theoretical maximum alkalinity for magnesium carbonate is pH 10·0. Dolomite soils may thus attain to greater alkalinity than limestone soils.

3. Alkalinity of over pH 10, due to sodium carbonate, may be reduced to pH 8 by the addition of calcium sulphate. The former reaction is injurious or destructive to vegetable cells, whilst the latter is favourable to most plants.

4. Soil acidity may be occasioned by the oxidation of sulphur from iron pyrites. This acidity favours the production of available phosphate, and is accordingly beneficial to certain plants.

5. Owing to production of carbonic acid by bacteria, a soil extract may decrease in alkalinity from pH 8·7 to 7·2, or less. The result in the soil appears to be to render iron salts more readily available in calcareous soil when inundated than when uncovered. The alteration is usually more rapid in soils from the top six inches than at greater depths.

6. Continuous manuring with sulphate of ammonium, or of potassium, decreases the effective soil alkalinity, even in a calcareous silt, but by a small amount only, about pH 0·2–0·4 in cases examined.

7. An acid soil extract is only slightly altered by boiling, from pH 5·4 to 5·7 in one instance. Alkaline extracts tend to reach the maximum value for calcium carbonate, pH 9·0. Higher values, such as pH 9·2, appear to indicate the presence of magnesium in small amount. The altered reaction is probably of importance in inhibiting the growth of certain soil organisms in heated soil.

8. When arranged in order of decreasing alkalinity, soils derived from different materials stand as follows :—Calcareous silt, limestone, sandstone, calcareous tuff (schalstein) with slate, slate, pillow lava (spilite), felsite, and granite. The values are modified in certain places, for proximity to the coast lessens acidity, and a high gradient often increases it. The results relate mainly to Devonian strata and accompanying volcanic or plutonic rocks.

9. Records are given for the hydrogen ion concentration of the habitats of over a hundred native plants. These show that this measurement is a valuable index of various soil conditions, and that many plants are limited to a short range of pH values. Others, with a wider range, occur mainly in one portion of it, but some plants grow well at widely different soil reactions. A distinction must be made between acid peaty soils, acid clay soils, and acid sandy soils.

10. The cultivation of wild flowers in a garden is dependent for its success upon the soil reaction of the natural habitats being maintained.

11. Natural waters, even from the peaty districts examined, contain no acid other than carbonic. Water in a spring may be at pH 6·4, and the stream flowing from it at pH 8·3, when in equilibrium with the atmospheric concentration of carbon dioxide. Photosynthesis may raise water containing magnesium salts to pH. 9·7. The method of limiting ionic concentrations may be applied to determine the amount of calcium carbonate in a soft water. This method shows Dartmoor water (R. Yealm) to contain 0·004 gram per litre of calcium carbonate in October. The hydrogen ion concentration of natural soft waters tends to increase during winter and to decrease in summer.

XXXI.

THE HYDROGEN ION CONCENTRATION OF PLANT CELLS.

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[Communicated by Professor H. H. Dixon, Sc.D., F.R.S.]

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Introduction.

An exact knowledge of the reaction of living cells is a necessity for the study of the chemical changes taking place in their metabolism. That this is so will be appreciated by a consideration of the influence of hydrogen ion concentration upon such changes as, for example, the molecular rearrangements of the sugars as studied by Nef (1911), or the rates of oxidation of sugars and of cystein (Mathews, 1909). In enzyme chemistry the controlling influence of the hydrogen ion concentration has been strikingly demonstrated by numerous researches, such as those of Sörensen (1909) upon invertase, catalase, and pepsin; of Michaelis (1909, 1914) upon invertase and malt diastase; of Bunzel (1916) and of Reed (1916) on oxidases; of Okada (1916) on the proteoclastic action of taka-diastase; of Frankel (1917) on papain; of Sherman, Thomas, and Baldwin (1919) upon three typical amylases; of Harvey (1920) on catalase in diseased leaves. Furthermore, the hydrogen ion concentration has been found to regulate the physical condition of proteins and similar substances; accounts of work in this line are given by Loeb (1918), Robertson (1920), MacDougal (1920), Cohn, Gross, and Johnson (1920), and Zoller (1921). For a full bibliography, that given by Clark (1920) may be consulted. It contains over eleven hundred references; and the list given by Schmidt and Hoagland (1919) has over four hundred and fifty.

No further emphasis need be laid upon the desirability of precise information on a factor so intimately concerned with the regulation of many processes of the cell.

As far back as 1902 Friedenthal applied the method of measuring electrical potential differences to the determination of the reaction of animal liquids. Its application to plant physiology came much later, though mentioned by Friedenthal (1910). But from 1916 onwards a number of determinations have been made, such as those of Haas (1916, '17, '19, '20); of Bunzel (1916); Reed (1916, 1 and 2); Hempel (1917); Kappen (1918); Patten and Mains, quoted by Clark and Lubs (1917); Truog and Meacham (1918); Fred and Davenport (1918); Clevenger (1919); Hoagland (1919); Swanson and Tague (1919). The results of some of these researches will be mentioned further on.

Hydrogen ion concentrations met with in plants.

From early work on the subject it was established that plant cells might be neutral or slightly acid to litmus, and the rather strong acidity of unripe fruits is well known. Hof (1909) used iodo-eosin as a test for free alkali in dried-up plant tissues; but results thus obtained are, it seems, highly misleading if taken to apply to the living plant.

The numerous electrometric and colorimetric researches already mentioned showed that plant-sap ranges from almost neutrality to pH 1·7, the value for lime juice, as given by Patten and Mains. Values for other fruits ranged from pH 4·5 downwards, viz. in the direction of greater acidity; but a lesser degree of acidity is met with in massive storage organs, such as potato tuber pH 6·2, sweet potato pH 5·7–6·6, beet pH 6·6. For those unaccustomed to think of acidity in pH values it may be of use to mention Wherry's (1919) suggested nomenclature for soil studies; this author takes the hydrogen ion concentration of pure water as unity. For this pH = 7; for a solution of acidity pH = 6, the "specific acidity" is 10, because the concentration in hydrogen ions is ten times as great as in pure water. Thus it may be seen that the "specific acidity" of lime juice, taking it as pH = 2, is as great as 100,000. It is 10,000 times more acid than potato juice. An even higher value, pH = 1·4, was found by the writer for an Indian berry, something like a gooseberry in appearance. For comparison it may be mentioned that the value for a centinormal solution of hydrochloric acid is pH = 2; yet this is usually considered a very dilute acid. For adult gastric juice pH = 1·8 approximately, and a solution of carbon dioxide in water nearly saturated at 25° C. is at pH = 4·8. On the other side the

pH value for sea-water is about 8·2; it is, therefore, slightly alkaline, or, in Wherry's terms, it has a specific alkalinity of over 10.

As far as the writer is aware, but few plant-saps are alkaline, and those only very slightly so, as, for example, the roots of wheat, as found by Kappen (1918). Haas (1916) has drawn attention to the fact that the sap may in some cases lie between pH 7 and 8. The writer has found some marine algae to be alkaline pH 7·3 or slightly less. Colorimetric work may, where clear sap solutions are available, be brought to much precision by the use of a Kober (1917) colorimeter, as pointed out by Duggar and Dodge (1919). The writer has found the Duboscq colorimeter very satisfactory for the purpose also. All researches based on electrometric or colorimetric estimations on expressed sap are open to possible sources of error in the changes undergone during extraction. For example, as shown by Mason (1920), leaves exposed to toluene vapour, in order to increase the permeability of the cells and to render the expression of the sap easier, are found to develop a considerable amount of heat owing to rapid oxidations. The well-known browning of many plant juices when expressed shows the influence of oxidation, which may alter the acidity. McClendon and Sharp (1919) record a change in carrot juice from pH 5·85 to 5·73 on standing twenty minutes in air. For this reason the work of Haas (1916) is of special interest, inasmuch as he uses the anthocyan pigments of petals as natural indicators of reaction in the living cell. It has frequently been assumed that a red colour denotes an acid cell-sap in the petal, and a blue an alkaline. Haas, however, extracted the pigments, and observed the colour given when in solutions of known pH. In this manner he showed that, for example, the pansy, which is blue, yields an anthocyanin which is rose from pH 1 to pH 4, blue at pH 5, and blue-green from pH 6–8. From pH 9–11 it is green, and finally yellow at pH 12. It is clear, therefore, that the living cells are in the neighbourhood of pH 5. It is accordingly not alkaline, but of well-marked acidity. The fading of colour in the cells as they die is accompanied by a decrease in acidity.

Determinations involving small quantities of liquid.

When only small quantities of liquid are available it is often allowable to dilute the solution sufficiently for the pH to be determined with very approximate accuracy. As pointed out by Clark (1920), under certain conditions the effect of dilution is almost negligible. This device may be employed with advantage for highly coloured or turbid solutions.

Haas (1919) made use of the comparison of drops of solution on white porcelain against drops of standard solution, with addition of a suitable

indicator, and of specially prepared indicator papers. Wagner (1916) previously employed the drop method, using lacmosol as indicator in work on plant immunity. Indicator papers were also used by Hempel (1917) in a research on succulent plants.

Felton (1921) has found this drop method very serviceable for work on tissue cultures, and thinks it preferable to working with 2–3 mm. tubes and diluted liquid, owing to dilution errors in fluids of low buffer action. It was also tried by Jameson and Atkins (1921) for work on the tissues of the silk-worm, and has been used by the writer for a year with, it is thought, fairly reliable results.

Determinations of hydrogen ion concentrations in plant tissues.

When working upon the hydrogen ion changes taking place in the course of the *mahai* or fermentation of indigo, it seemed desirable to see what relation the final stage (which was at about pH 5·6, as far as could be judged in the brownish liquid of a small-scale fermentation) bore to the acidity of the indigo leaf. It may be remarked that the initial value was about pH 8·5, i.e., that of the river-water. The plan adopted was to crush portions of indigo leaf on white porcelain, with the addition of one or two drops of distilled water, and to compare the colours given with methyl red and brom cresol purple against those which appeared with the standard buffer solutions. It is always advisable to use two indicators where possible, as it lessens the chance of any serious error. In this way it was found that the leaves of young and old plants were of acidity pH 5·6, whereas cotyledons still in the seed-coat were slightly less acid, pH 5·8. Determinations were thus made upon various Indian plants, and are recorded elsewhere (Atkins 1921). In addition to working with crushed tissues, an attempt was made to use the indicator on sections in order to see whether adjacent cells differed noticeably in acidity, for it seemed possible that in crushing a stem the result might give a very misleading idea of the true condition of the conducting tracts.

For example, it was found that varieties of the castor-oil plant (*Ricinus communis*), grown at Pusa, gave pH 4·6 for the stem, for both red- and green-stemmed plants, but the tissues were not examined separately. It was similarly found that young leaves, older leaves, and a young flower were at pH 4·8. A section across the seed-capsule with very immature seeds showed, however, that the wall tissues were at pH 4·8, while the seeds were much less acid, pH 5·4. Had the capsule been crushed, an erroneous result would have been obtained. The acidity of the crushed pollen sacs was also pH 5·4, as nearly as could be judged.

These values are at least comparable ones, though on account of the presence of proteins in the cells an error is introduced. The indicators used, however, were selected by Clark and Lubs (1917) as having small errors from this source, as has been further demonstrated by Homer (1917) in serum studies.

The application of the method to the mapping out of the acidity of tissues may be illustrated by the following :—

The Labiate *Salvia Verbenaca* grows plentifully near the Plymouth laboratory, and affords convenient material. A fresh transverse section of the stem was stained with various indicators, and it was seen that di-ethyl red (Lubs and Clark, 1915) gave with the pith a yellowish colour, which was also seen in the medullary rays and cambium. The wood was a good red in the walls ; the bast fibres were deep red in the cells, as were also the cells of the sclerenchyma in the four angles of the stem. The cortical parenchyma between the bast fibres and assimilating cells was yellowish ; the assimilating cells were apparently a very light yellow, as far as could be judged in the presence of the chloroplasts. The epidermis was seen to be a deep red, but this is its natural colour; to avoid error it is always necessary to examine an unstained section.

Since di-ethyl red changes from red to yellow between pH 5·8 and 6·0, it is at once clear that the red-stained portions must be at least as acid as pH 5·8, and the yellow equal to or less acid than pH 6·0.

Using methyl red, the sclerenchyma and bast fibres give a salmon pink to pink colour, corresponding to pH 5·4 to 5·2 ; the wood appears a faint pink, not more acid than pH 5·4 to 5·6, and the medullary rays are yellow. The upper limits of acidity are therefore fixed.

It remains to determine the acidity of the portions appearing uniformly yellow of the same tint with di-ethyl red. With phenol red the full yellow colour appeared, showing an acidity of pH 6·6 or more. With brom thymol blue a yellow with a green tinge was seen, matching the colour with pH 6·2. A green tinge in the tissue may, however, make this acidity slightly too low. Accordingly a small cube of the medulla was excised with a stainless steel knife, which was found very useful for this work, and was crushed in a watch-glass with an agate pestle, and to this one drop of the dilute brom cresol purple was added. The tint was matched by taking two drops of standard buffer solutions, pH 5·8, 6·0, and 6·2, with one drop of the reagent, since the volume of the crushed tissue was closely the same as that of two drops. The colours were pH 5·8 dirty greenish, 6·0 slaty blue, and 6·2 deep slate blue. The medullary tissue was a very close match to 6·0.

Thus the various tissues seen in the cross-section of this stem with the

aid of a hand lens or low-power (two-thirds inch) objective have been mapped out with tolerable accuracy as lying betwen pH 5·2 and 6·0. The results may be summed up as follows, the C_H values corresponding to the pH values being also given, to emphasize the magnitude of the acidity differences involved:—

	pH	C_H
Sclerenchyma and bast fibres, . .	5·2–5·4	$0{\cdot}63–0{\cdot}40 \times 10^{-5}$
Wood walls, ...	5·4–5·6	0·40–0·25 „
Medullary rays, medullary and cortical parenchyma, ...	6·0	0·10 „

Thus it is seen that the acidity in the sclerenchyma is four to six times as great as in the adjacent cortical cells, but, on account of the relatively great bulk of the parenchyma, expressed sap would appear to be more nearly of the acidity given by the latter. This relatively high acidity of the wood and sclerenchyma seems to be quite a normal occurrence, and cannot fail to have a physiological significance.

As a further example of the difference in reaction between portions of a plant in fairly close proximity may be mentioned the behaviour of wheat seedlings (Pusa 4 variety). These were removed from soil with a strongly alkaline reaction, pH 8·8, and the roots were washed till the washing water gave pH 7. The roots then were at pH 6·8, as shown by brom thymol blue and phenol red. The white leaf bases and the young green leaves were both at pH 5·4, as shown by methyl red and brom cresol purple. As already mentioned, Kappen (1918) found cereal roots neutral, those of wheat even being slightly alkaline. At Pusa the roots were slightly on the acid side of neutrality for wheat, an identical value being given by those of both oats and rice, viz. pH 6·8. The leaves of the oats were at pH 5·4, while with the rice the leaf gave pH 4·8, the first and third internodes of the stem being at pH 5·0, intermediate with the value of the roots.

With a very simple outfit it is possible to make determinations of the acidity of plant tissues in the field. This is of value in work correlating the acidity of the plant and the soil, and in cases where for any reason a laboratory is not to hand. A few small tubes of the necessary indicators are required, one or more glass rods, and a few watch glasses. It is also well to have a knife of stainless steel, a hand lens, and a bottle of distilled water, or of rain water. On such expeditions a separate reprint of the coloured chart of indicators at various pH values given by Clark is very useful, and the buffer tablets already mentioned are a desirable item, and add little to

the weight. It is necessary to test the bottle used for water to make sure that it does not give off an appreciable amount of alkali during the course of the work. It is found that the ground-glass region of the stopper is specially liable to cause trouble of this sort. It is, therefore, preferable to remove water with a pipette and rubber teat rather than to pour it out. With a little experience as to the tints given by the indicators it is possible to work with approximate accuracy of pH 0·2 to 0·4 with the aid of the chart. As a rule the determinations will be accurate to pH 0·2 or less, especially if use is made of two or more indicators. If buffer tablets are carried, the work can be as precise as in a laboratory. As an example of such determinations, the following may be mentioned:—

Anagallis arvensis, transverse and longitudinal sections of the stem stained red in the vascular bundles and yellow in the pith with methyl red. The former was, therefore, more acid than pH 5·2, and the latter less acid. Di-ethyl red was not available at the time, so the lower limit was not determined, but it was at least pH 5·8.

Taraxacum officinale, transverse section of stem showed pH 4·6; latex abundant; rootstock latex canals pH 4·4–4·8; vascular bundles much the same, but not quite as acid as the latex, which gave a more purple tint with methyl red; rootstock medulla pH 5·4. Leaf parenchyma lay close to pH 5·8, as shown by brom cresol purple, and by its yellow colour to methyl red, whereas the midrib was about pH 4·6.

Cochlearia armoracia, transverse section of stem was at pH 4·6 in vascular bundles and sclerenchyma, pH 6·0, or slightly less acid, in parenchyma. The leaf parenchyma was at pH 5·4.

These three plants were growing in soil which gave with water pH 7·6–7·2, as shown by phenol red.

In conclusion it may be mentioned that in cases in which the sap is coloured, or the crushed material is turbid or milky, it is sometimes useful, having made an approximate determination of the pH value with indicator and drops of standard buffer solution, to try adding the buffer solution of the nearest pH value to a portion of the crushed tissue. Since the buffer action of the plant sap, whilst by no means negligible, as shown by Hempel (1917), is not at all as great as that of the added solution, the alteration of the pH value of the latter can be but slight with sap of approximately the same pH value. The resulting colour of the true pH is, however, modified by the tint or turbidity of the tissue, and thus a good match may be obtained with the plant sap. This is especially useful with dichroic indicators, such as brom phenol blue and brom cresol purple.

Hydrogen ion concentrations of plant secretions and exudations.

It seemed of interest to study the reaction of the transpiration stream, since, owing to the fact that it is evaporated in the leaves, the acidity, if any, would be concentrated in course of time. The determination is not easily made, since even if a woody stem is cut and centrifuged (Dixon and Atkins, 1915) there is the risk of contamination with the sap of living cells, and this, though diluted, might cause an appreciable error. It is hoped, however, to test this by direct experiment, and to see whether the variation in sugars previously shown is accompanied by any change in acidity.

Recourse was had to the liquid which drips from the leaf tips of *Colocasia antiquorum*. Attention had been drawn to the great purity of this water by early workers, Duchartre (1859) and Musset (1865), and a plant growing in the Trinity College, Dublin, Botanic Gardens was found by Dixon (1914) to have a freezing point indistinguishable from pure water when tested by the thermoelectric method, one couple being in each of the two liquids. Further, the electrical conductivity was less than that of Dublin tap-water, a very soft upland water from a granite and quartzite area. The solids amounted only to 0·012 per cent. as determined by evaporating 20 c.c. of the liquid. It had also been shown by Miss Flood (1919) that this liquid is in direct connexion with the conducting tracts of the leaf, and has therefore passed through living cells only in the roots. The colorimetric determination with brom thymol blue, using 10 c.c. of the liquid which issues from the leaf tips, gave pH 6·8, which is a value given by distilled water quite frequently owing to the absorption of carbon dioxide. With the same indicator it was found that sap pressed from the leaf stalk was at pH 5·4, and the leaf tissue at 6·0. It is clear, therefore, that this water of the transpiration stream is entirely uncontaminated with acids, though it has passed through the root tissues and the conducting tracts of the entire plant.

Another liquid of interest is the water found in the axils of the leaves of *Dipsacus laciniatus*. This has been shown by L. B. Smyth (private communication) to be without digestive action. A plant growing in the Botanic Gardens was found to contain much water in the axils. This was at pH 6·8 in a lower leaf and 7·0 in an upper one. The lower one contained dead flies. Since the water was present after a considerable period of drought, it is clearly derived from the plant, and is quite possibly in connexion with the conducting system. This point was not, however, investigated.

The pitchers of *Sarracenia* spp. are also well known to contain liquid. It is stated that this is without digestive action, but that insects caught in it

are decomposed by bacteria and the products absorbed. It, therefore, seemed probable that this water would be nearly neutral in reaction. Pitchers of *Sarracenia purpurea* × Hort., in the Botanic Gardens, were examined, and an old one was found to give a red colour with phenol red, denoting an alkaline reaction. This, however, may have been due to chance contamination, such as from a flake of whiting from the windows, for it was found that young pitchers contained a clear colourless liquid of pH 5·0 to 5·2, as shown by methyl red. Older pitchers of *S. tolliana* × Hort., varied from pH 6·0 to 6·8 when tested with brom thymol blue. It was subsequently discovered that Wherry (1920) had tested this liquid in several species growing wild in the swamps of the middle Atlantic States of the U.S.A. He found that the liquid in the pitchers was usually "mediacid" or "subacid," namely, pH 4 to 5 and pH 5 to 6 respectively. He attributed the acidity chiefly to carbonic acid, but, though a saturated solution is in the mediacid region, it would soon lose carbon dioxide, so another acid must be present. Where the reaction was found to be between pH 6 and 8, he considers that calcium bicarbonate had dropped into the upturned pitchers from leaves of other plants which drew from alkaline water supplies. The *Sarracenia* plants were always on acid hummocks when the soil around was alkaline. It has, however, been shown by Hepburn (1918) that the unopened pitchers of *Sarracenia* are sterile, and the liquid has a proteolytic enzyme; in older opened pitchers bacteria are symbiotic. It is, therefore, not at all surprising that the contents of the pitchers should be acid when freshly opened, and it may be that the alkaline reaction found in some, both by Wherry and the writer, is not due to chance contamination, but to the products of digestion, or to those of bacterial action. Bodine (1921) has proved that protozoan cultures in hay or soil infusions change in time from an acid to an alkaline reaction. Possibly the old pitchers alter owing to the development of protozoa. This could be tested directly.

An attempt was made to examine the liquid in pitchers of *Nepenthes sp.*, as this is known to have a digestive action, but unfortunately the pitchers were dried up. *Drosera binata*, Labill., was, however, plentiful, and the leaf-hairs were well covered with the characteristic beads. On touching with a glass rod and stirring with water on a watch-glass it was observed that it was hard to get these mucilaginous droplets to mix. With brom thymol blue and phenol red the reaction given was pH 7·0, but the former indicator showed pH 6·4 when tested with the liquid round a dead fly. Thus it appears that acid may be secreted only when the hair is stimulated, or it may have come from the fly.

D. rotundifolia was obtained growing on Dartmoor, and on washing the glandular leaf-hairs with a drop of water they were found to be quite strongly acid, pH 4·8, or slightly more acid using methyl red. The crushed leaf was carefully compared with standards, and agreed with pH 3·0, using brom phenol blue. This was confirmed with thymol blue. The significance of this in connexion with enzyme action will be mentioned later.

Relation of the natural acidity of plant tissues to the activity of their enzymes.

Determinations made on the fruit of *Carica papaya* at Pusa showed that the latex of the skin of the unripe fruit was as acid as pH 5·4, an identical value being given by the hard central tissue. On looking up Frankel's (1917) work on purified commercial papain, it was seen that this enzyme works most rapidly at pH 5 when the temperature is 37° C. Taking this rate as 100, the rates from pH 3 to pH 7 are respectively 27, 91, 100, 63, 47.

The natural reaction of the fruit is, therefore, close to the optimal value for papain action. According to Kilmer (quoted from Mendel and Blood, 1910), the ripe fruit gives no latex when the skin is cut, and the pulp shows very little proteolytic activity. Unfortunately no ripe fruits were available for the examination of pH values. The marked action of hydrogen cyanide in activating papain, especially as regards the progress of the action up to the formation of amino-acids, as described by Mendel and Blood, may, perhaps, be of significance in the physiology of plants having cyanophoric glucosides.

Again, the recent work of Falk and M'Guire (1921) has shown that the action of soluble sucrase from bananas is most active at pH 3·5 to 4·5. Taking the activity at pH 4·0 as 100, the series at intervals of pH 0·5, from pH 3·0–6·5, is as follows :—37, 98, 100, 98, 94, 78, 27, 11, the rates being measured at 35° C. In this case also the reaction of the fruit lies in the neighbourhood of the optimum for the enzyme, a freshly picked small unripe fruit being of acidity pH = 4·6–4·8, that of the skin being 4·6 approximately. For the leaf-stalk a value pH 4·9 was found. The pulp and skin of a fully ripe banana, examined in England, were found to lie between pH 5·6 and pH 6·0 in different cells. In considering the optimum pH value for any enzyme, account must be taken of the temperature, for Compton (1921) has shown that the optimum value varies with the latter. Thus, for the maltase of *Aspergillus oryzae*, he found that for pH 3·0 the maximum hydrolysis occurred at 35·5° C., whereas at pH 7·2 it was not reached till 47° C. In the natural conditions of growth of the papaw and banana at Pusa, an air temperature in the shade of 35°–38° is quite normal, and in full sunlight the fruits, in spite of surface evaporation, must often attain considerably greater temperatures. When one considers that the action of maltase at

pH 3 has fallen from its maximum rate at 35·5° C. to about two-thirds of this rate at 39° C., and to roughly one-third at 42° C., the importance of high temperatures combined with high acidity is made clear. With lower acidity, however, the optimum has not been reached at 42° C. It is thus very natural that the reaction found for the plant tissue should be rather below the optimum acidity for 35·5° C., since the fruit is certainly exposed during its development to higher temperatures at which a degree of acidity optimal for 35·5° C. would have serious destructive action on the enzyme. In tropical climates the black bulb thermometer may reach 72° C.; and it has been found that thermometers placed inside small wooden frames about a foot square and two inches deep, covered with linen, aeroplane dope, and varnishes of various colours, quite commonly reach 50°–60° in sunlight. These measurements were not made to investigate fruit temperatures, but they serve to show how high are the temperatures that may be found under such atmospheric conditions. It accordingly seems reasonable to suppose that temperatures of 45°–50° may be met with in ripening fruit in the tropics. In England during full sunshine in July it was found that with an air temperature 25·1° C. an untreated mercury thermometer rose to 33·7 when insolated; and a similar thermometer inserted in a ripe banana reached 33·4°. The fruit is thus over 8° above air temperature; and in view of the fact that in Upper Egypt and the Sudan temperatures of 44° are common, it is unlikely that 50° is at all too high an estimate for the temperature to which fruits in tropical climates may be exposed. In this connexion the decrease in acidity of fruits as they ripen is to be noted, and as the ripening usually takes place in the hot weather, it is possibly advantageous for enzyme action that the initial higher degree of acidity should be reduced.

As previously mentioned, immature castor-oil seeds were found to give a reaction of pH 5·4, though the leaves were at pH 4·8. No details, quite parallel with those on papain, of the effect of various pH values on lipase action are to hand; but Armstrong and Gosney (1913, 1914) have shown that after the enzyme has been liberated from its zymogen by dilute acetic acid, the low acidity of oleic acid is most favourable to its action. A table given by these workers shows the action of 0·5 gram of castor bean lipase upon a solution of ethyl succinate according as increasing amounts of various acids were present. The percentage hydrolysed in twenty hours was 56·5 with no added acid, as against 60·5, 61·8, and 57·3 with N/40, N/20, and N/10 butyric acid respectively, and 8·1 per cent. with N/40 sulphuric acid. If one neglects the quite possibly considerable effect of the enzyme preparation in diminishing the hydrogen ion concentration, though acid itself, and determines the pH values corresponding to the above concentrations, it is found that the butyric acid values are pH 2·67, 2·85, and 2·93, arrived at by

interpolation between standard solutions at 2·60, 2·75, and 3·0 with thymol blue. For the sulphuric acid pH 1·7 was obtained. Thus, at the temperature of the laboratory this degree of acidity had a very destructive action on the enzyme. As pointed out, the pH values recorded here can only be upper limits for the acidity actually in contact with the enzyme. In this connexion the work of Falk (1915, 1917) is also of interest. He found lipolytic enzyme from castor beans could be separated into an albumin-like body more active towards ethyl butyrate than to glyceryl triacetate, and a globulin-like body more active to the latter. It was ascertained that after standing for a day at 0° C., in a liquid of acidity pH 3·5, the esterase had almost become inactive when tested subsequently by its hydrolytic activity at 38° C. At pH 4·5 one-third of its activity had been lost. The destruction of the lipase was not quite as great. It was further proved that after standing for a day at 0° at pH 8 the esterase was slightly less active than at pH 7, but at pH 11 it had lost 90 per cent. of its activity.

Thus it is evident that the destructive action of an acidity of pH 4·5 at 0° upon lipase must stand in close relation to the fact that in the seed the reaction of the stem and leaf, namely pH 4·6, is found to be reduced to pH 5·4, a change of $C_H\ 0{\cdot}32 \times 10^{-4}$ to $C_H\ 0{\cdot}04 \times 10^{-4}$, namely to one-eighth.

Indicators for use with plant tissues.

Of the very numerous substances which act as indicators, Sörensen (1909) selected a limited number as giving well-defined brilliant colours, and being relatively uninfluenced by salt and protein errors, whereby a discrepancy arises between the true hydrogen ion concentration as shown by the potential difference method and the colorimetic method. Sörensen excluded cochineal, Congo red, alizarin, and all litmus preparations. He included neutral red, which is remarkably free from the errors, and is of great value by reason of its penetration of the living cell without toxic effects when in moderate concentration, for which purpose it was originally introduced by Ehrlich. This indicator gives a good clear red from pH 7·0 to 6·6, and the more acid region. It is reddish from 7·2 to 7·6, and orange beyond that. The stain is of special use in testing the reaction of algal cells in an alkaline medium, as will be described in detail elsewhere.

Clark and Lubs (1915, 1917) introduced the phenol sulphone phthaleins for use as indicators, and selected the best. All those shown in Clark's list are of value, and by reason of their stability and ready solubility in water as sodium salts, as well as their brilliancy, they are to be preferred to some on Sörensen's list. They include methyl red, introduced by Palitzsch (1911), which, though not readily soluble, covers a range much used. Clark and Lubs aimed at reducing the number of indicators, and this has naturally

many advantages, when dealing with clear solutions especially. However, with plant sections and drops of liquid a somewhat larger selection of indicators is very useful. For example, though the range from pH 5·4 to 6·0 is covered both by methyl red and brom cresol purple, yet for the greater portion the tints are yellowish. This is not readily observed in tissues, hence the value of di-ethyl red introduced and found reliable by Lubs and Clark (1915), but excluded later as unnecessary. This changes from yellow at pH 6·0 to red at 5·8, the colour increasing in depth with increase of acidity. Furthermore, it is readily taken up by those plant tissues with which it gives a red colour, whereas brom cresol purple is not well retained. On the more acid side the useful range of methyl red ends at pH 4·4, at which point brom phenol blue is blue. Methyl orange is often of service for greater acidity, especially as brom phenol blue is dichroic. The former is yellow at pH 4·6, and varying shades of orange to 4·0; at 3·8 and 3·6 the red predominates, and beyond 3·4 it is clear red. This is just the region in which the dichroic blue has become a yellow, and so difficult to observe in a section. The colours and ranges mentioned apply only to the dilutions found suitable for colorimetric work.

Summary.

1. Plant cells are rarely alkaline, and pH 8 is not surpassed in them. On the acid side pH 1·4 has been observed.

2. By a microchemical method it is possible to determine the pH values of the cells and tissues. It has been found that the xylem is more acid than the pith and medullary rays, and the midrib of a leaf more acid than the parenchyma. Parenchymatous tissue is often in the neighbourhood of pH 6; woody tissue nearer pH 5, or more acid. When grown in neutral or alkaline soil, the root is usually less acid than the other portions of the plant. The influence of soil reaction is reserved for consideration in another paper.

3. The transpiration stream in *Colocasia antiquorum* is almost neutral, as is also the liquid in the leaf-base troughs of *Dipsacus laciniatus*. The pitchers of *Sarracenia spp.* may be as acid as pH 5, and the glandular secretion of *Drosera rotundifolia* may be even more acid.

4. It has been pointed out that the pH value met with in a tissue is usually near, but slightly less than, the optimum for the activity of the characteristic enzyme at ordinary air temperature. This ensures that the acidity does not destroy the enzyme at such higher temperatures as may be experienced by the plant under natural conditions.

5. Attention is drawn to the usefulness of di-ethyl red as a reagent for microchemical work, as it gives a red in a region where methyl red and brom cresol purple are yellowish; in this range many plant tissues are found to lie.

XXXII.

NOTE ON THE OCCURRENCE OF THE FINGER AND TOE DISEASE OF TURNIPS IN RELATION TO THE HYDROGEN ION CONCENTRATION OF THE SOIL.

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It has long been known that the disease occurs in soils poor in calcium salts. Hall (1910) has collated the results obtained by Voelcker and other workers, which show that finger and toe was found on turnips growing in soil containing calcium, expressed as oxide, to the amounts of 0·14, 0·08, 0·13, 0·31, 0·39 per cent. in five cases studied, whereas spots, some in the same fields, with 0·89, 0·52, and 0·43 per cent. were free from it.

The writer is indebted to Mr. T. Sherrard, Maryborough, Douglas, Cork, for the notes on the behaviour of two fields and for soil samples.

1. "This sample is infested very badly with finger and toe. No turnip or cabbage can grow in this soil."

2. "This sample is from the same land, only a stream of water dividing the fields. No trace of finger and toe is found here. It is absolutely free from fungus, and grows fine turnips."

Sieving showed that in each pebbles, &c., which did not pass 30 mesh to the inch, amounted to 23 per cent. of the air-dry soil. Of the good field, 65, and of the bad, 64 per cent. passed the 100-mesh sieve. The soil which passed the latter was found to contain 0·17 and 0·40 per cent. of lime in samples Nos. 1 and 2 respectively. In view of previous work, it is safe to attribute the behaviour of the two fields to their difference in calcium salts. The good field is, however, rather dangerously depleted, as Hall records disease in sandy soil with 0·31 per cent. of calcium oxide, and in clay soil with 0·39. The addition of lime or limestone to the bad field is clearly indicated, and it would probably benefit the other also.

The acidity of these soils was determined by the colorimetric method, as described and explained in a previous paper (Atkins, 1921). It was observed that the reaction was only very slightly different, the good field being less acid by an amount estimated at pH 0·1, using brom thymol blue and brom cresol purple as indicators. With neither was there

any doubt that the soil of the bad field was the more acid. Using brom thymol blue and the Clark and Lubs standard buffer solutions, which are at pH 0·2 intervals, it was seen that No. 1 was at pH 6·6, and No. 2 at pH 6·7, or slightly more, not up to 6·8. The difference appeared somewhat less with brom cresol purple. The actual numerical concentrations of hydrogen ion are respectively C_H 0·25 and 0·20 × 10^{-6} gram per litre.

It would be of interest to study a large number of samples, and it is hoped that this may draw attention to the value of the method, since, once the standards are prepared, it is very rapid, and comparisons can be made even without standards. Neutrality at 16° C. is at pH 7·1, and it is probably safe to conclude that a soil giving pH 6·9 or 7·0 will not be liable to have its turnip crop attacked, unless possibly when subjected to heavy infection through manure from animals fed on diseased turnips. It may be mentioned that cabbage as well as turnips failed completely on the No. 1 soil, though basic slag was used with both in successive years. This soil will grow nothing if touched in wet weather; a crop of mangolds was lost in trying to work it when wet. It gets sticky and then hardens, when nothing will grow. It seems that the texture of this clay soil would also be improved by liming, as the colloidal particles would be clumped thereby.

It would be of interest to make a biochemical examination of diseased and healthy plants to try to ascertain how it comes about that a deficiency in calcium salts renders the plant more susceptible. Possibly the effect is, in part at least, upon the fungus, which refuses to grow in a neutral or slightly alkaline medium. This statement, quoted from Hall (1910), is based on work done prior to the introduction of the present methods of determining hydrogen ion concentrations, so it would be of interest to ascertain the limits between which the fungus can be grown.

No direct proof has been given that the pathogen was present in the No. 2 field, and the conclusion put forward has been criticized on this score. In view of Hall's work, however, it seems to the writer that there is at least a reasonable degree of probability in favour of the presence of the pathogen, and further work will show to what extent the pH limits given here must be modified.

Summary.

One of two adjacent fields of similar clay soil was found to be badly infested with, and the other free from finger and toe disease in the turnip crop. It was found that they contained, respectively, 0·17 and 0·40 per cent. of calcium, calculated as oxide. The hydrogen ion concentration of the samples was pH 6·6 and pH 6·7, or slightly over, respectively, as determined colorimetrically, or, stated otherwise, C_H 0·25 and 0·20 × 10^{-6} grams per litre respectively.

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XXXIII.

PHOTOSYNTHESIS AND THE ELECTRONIC THEORY (II).

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It has been pointed out that the energy required in photosynthesis to form carbohydrates from carbon dioxide and water is derived from the light energy rendered available by the displacement of electrons of the chlorophyll molecule. This view is necessitated by the fact that the wave frequencies absorbed by chlorophyll are those which are effective in photosynthesis (1).

Previous experiments have shown that the number of electrons ejected from the molecules of chlorophyll when illuminated by visible light could not carry anything like sufficient energy to make the formation of the observed quantities of carbohydrates possible external to the chlorophyll. Hence it would seem to follow that the necessary electrons are not ejected from, but are merely displaced in the chlorophyll molecule (1). This displacement may be supposed to render some atomic group in the chlorophyll molecule reactive leading to the fixation of carbon dioxide, to the separation of a carbohydrate from its complex molecule, and to reconstitution of the original from the residue and water, with the evolution of oxygen.

This paper contains an account of some experiments carried out with a view to testing further the photo-electric properties of chlorophyll by means of a photographic method.

According to the generally received view, the latent image of the photographic film is formed by the displacement of electrons on exposure to light. The development of the plate reveals the ionization so caused, and converts the latent image into the photographic image. A strong confirmation of this view is to be found in the observation that the latent image may be formed at a temperature so low that no chemical action is possible (2).

An extension of this theory explains the action of sensitizers. Light of wave frequencies, which are unable to form a latent image in the untreated

film, may be rendered effective by tinging the film with a dye which absorbs those wave frequencies. Here the electrons of the dye-molecules displaced by the absorbed light are regarded as the cause of the ionization necessary to form the photographic image on development.

This view would receive additional support if it could be shown that sensitizers are effective at temperatures at which chemical actions do not take place.

Sensitization at Low Temperatures.

To test this point experiments were made on the following lines. Ilford process plates, which are comparatively insensitive to red light, were cut up into a number of small plates, 1 cm. × 2 cm. Half of each of these was sensitized by immersing it for a few seconds in a solution of "Sensitol Red" (1 : 76,000), as supplied by Ilford, Ltd., and made up according to the maker's directions. After the plates had dried, one was attached to a disc of blackened cardboard (the "back"), 2 cm. in diameter, by a rubber band passing lengthwise across the plate, and at right angles to the line of junction between the sensitized and untreated portions of the plate. The back was then fixed at one end of a blackened cardboard tube, about 30 cm. long, the other end of which was closed with a transparent Wratten light filter, No. 29, transmitting only red light of wave-lengths greater than 615$\mu\mu$. The cardboard tube, which formed a long camera, was set upright in a flask-shaped Dewar vessel, so that the lower end containing the back was submerged in the liquid air held in the vessel. The upper end projected from the neck. The liquid air in the vessel, entering by perforations in the lower part of the tubular camera, covered and completely submerged the plate. The Dewar vessel and camera were set directly under a 100-watt "gas-filled" lamp. The plate was about 40 cm. distant from the lamp. All these arrangements and operations were performed in total darkness. Exposure was made by switching on the lamp. Exposure for one hour under these conditions produced a latent image, which on development with rodinal showed only a slight silver deposit on the untreated portion of the plate. A clear strip—the shadow of the rubber band—without silver deposit crossed this portion. The rest of the plate which had been sensitized showed out dark in contrast; but it, too, was crossed by the clear shadow.

This experiment, which was frequently repeated, shows conclusively that the sensitizer is effective at the temperature of liquid air (−185° C), and hence supports the electronic theory of sensitization. There is, however, a marked loss of sensitiveness at this temperature, for a control plate with precisely the same arrangements, save that the flask did not contain liquid

air and was at room temperature, showed a stronger deposit of silver after thirty seconds' exposure than did the experimental plate after an hour's exposure. Furthermore, it should be noticed that the effectiveness of the sensitizer is considerably reduced at this temperature, for it is always observed that the contrast between the sensitized and untreated portions is much greater on the film exposed at room temperature than on that submerged under liquid air during exposure.

These experiments show that the photographic film may be used as a means of testing the electronic disturbances caused by light in substances distributed through it. It will be noticed that the effects on the film will be summative, and, therefore, given time, even when the number of electrons displaced per second is small, sensible effects may be produced.

Sensitization by Chlorophyll.

It is well known that chlorophyll, like many dyes, acts as a sensitizer to the photographic film, and the fact that its presence renders the photographic film sensitive to those wave frequencies which it absorbs is strong evidence that, in its case also, exposure to light leads to the displacement of electrons. This conclusion would be rendered almost certain if sensitization by chlorophyll could be shown to be effective at the temperature of liquid air.

Nearly all experimenters on photographic sensitization by chlorophyll comment on its uncertainty. The uncertainty of its action is particularly noticeable when it is used in conjunction with gelatine photographic films. As gelatine plates are so manageable, and give such excellent results with other pigments, it seemed worth while to carry out some experiments to try and ascertain the conditions necessary for their sensitization.

Experiments on the Sensitization of Gelatine Films.

Untreated photographic gelatine films were immersed in alcoholic extract of fresh leaves, alcoholic extract of dry leaf-powder, and alcoholic extract of leaves killed by exposure to steam. None of these preparations of crystalloidal chlorophyll gave certain results.

Similarly untreated plates immersed in or smeared with colloidal chlorophyll were equally uncertain.

The addition of different quantities of ammonia to the sensitizing bath—although some good plates were obtained by this method—did not render sensitization certain. Neither did the acidulation of the bath produce better results.

An effort to change the sign of the colloidal chlorophyll by the addition of calcium sulphate did not secure sensitization.

The reverse process was also tried, namely, to change the sign of the gelatine of the film, but it was found that plates soaked in a solution of barium nitrate were no more easily sensitized than untreated ones.

The influence of the physiological condition of the chlorophyll itself was also tested; thus extracts from leaves recently exposed to light were compared with those made from leaves previously shielded from light. No difference was observed. In the same way extracts made and stored in darkness showed themselves no different from those which had been exposed to the light.

These preliminary experiments afforded no hopes that certain results could be readily obtained with gelatine photographic plates. Consequently it was decided to abandon gelatine films and to carry out the experiments with collodion emulsion in spite of its inconveniences.

It was noticed, however, that in the occasional cases in which satisfactory sensitization was obtained with gelatine plates it was effective, not only at room temperature, but was also observed on portions of the same plates exposed under liquid air.

Experiments on the Sensitization of Collodion Films.

The first experiments which we made with collodion were carried out with an emulsion made up in the laboratory. The plates, which were coated and allowed to dry for about five minutes, were then immersed in a leaf-extract. Subsequent drying lasted half an hour, and then the plate was exposed to light, as previously described in the case of the gelatine films, at room temperature for sixty to eighty seconds. Sensitization was easily obtained both with ordinary dry-leaf extract and with an alcoholic solution of chlorophyll *a* and *b* purified from the accompanying yellow pigments and fats.

With exposures for thirty minutes and sixty minutes under liquid air the result was inconclusive, as the whole plate appeared somewhat fogged, and no clear strip corresponding to the shadow of the band was observed.

Similar collodion plates sensitized with "Sensitol Red" in a similar manner gave good results, both for room temperature and when submerged in liquid air. At room temperature (as in the case of gelatine plates) the effectiveness of the sensitizer, as shown by the contrast between the sensitized and untreated portions of the plates, was much greater.

Further experiments were carried out, using a sample of collodion prepared and supplied by Messrs. Johnson & Sons, Finsbury, London. The coated plate after five minutes' drying was partially immersed in leaf-extract. After this immersion it was again allowed to dry for ten to fifteen minutes. Exposure to light for three hours was then made while the plate was submerged in

liquid air. On development satisfactory sensitization was apparent. The development with rodinal lasted in each case about three minutes.

These results, which were repeated several times, establish the fact that sensitization with chlorophyll of photographic films, whether of collodion or of gelatine, is effective at the temperature of liquid air. Inasmuch as in these experiments it is only light of visible wave-lengths, viz., $\lambda = 615\mu\mu - 725\mu\mu$, which is absorbed by the chlorophyll, and produces the ionization forming the latent image, it follows that this light displaces electrons of the chlorophyll. Previous experimental work has shown that visible light does not expel electrons from chlorophyll.[1] Hence it follows that the energy absorbed from visible light is wholly or in part used in the displacement of electrons within the chlorophyll molecule, making some atomic group or groups within it reactive. In photosynthesis, we may suppose that these groups react with the raw supplies, viz., carbon dioxide and water.

We might imagine the process to take place as follows :—

$$\underset{\text{(chlorophyll } a\text{)}}{C_{55}H_{72}O_5N_4Mg} + CO_2 = \underset{\text{(chlorophyll } b\text{)}}{C_{55}H_{70}O_6N_4Mg} + CH_2O$$

$$\underset{\text{(chlorophyll } b\text{)}}{C_{55}H_{70}O_6N_4Mg} + H_2O = \underset{\text{(chlorophyll } a\text{)}}{C_{55}H_{72}O_5N_4Mg} + O_2.$$

Such a scheme would account for the constant proportions of chlorophyll *a* and *b*. The fact that the formation of formaldehyde cannot be detected when chlorophyll in presence of carbon dioxide alone is exposed *in vitro* (3) may be explained by assuming, with Siegfried (6) and Willstätter (8), that the fixation of carbon dioxide with a protein is first necessary, and that the decomposition of the carbamino-acid or carbaminate is effected by the reactive group in the chlorophyll produced by the absorption of light. The formation of chlorophyll *b* and formaldehyde from chlorophyll *a* and this loosely combined carbon dioxide would probably take place instantaneously on exposure to light. A momentary inflow of carbon dioxide to make up the loss of carbamino-acid or carbaminate might be expected; but the subsequent rate of absorption would depend on the rapidity with which the carbamino-acid was broken down by the available chlorophyll *a*, and would gradually rise to a steady state as the normal proportion of chlorophyll *a* to chlorophyll *b* was

[1] It is of interest here to record an unpublished observation of J. Joly and J. H. J. Poole. These investigators, using an extremely sensitive method of investigation—the tilted leaf electroscope—found that another sensitizer, viz., Sensitol Red, like chlorophyll, is practically non-photoelectric under the action of visible light.

re-established. Such a rise in the rate of photosynthesis during illumination, as determined by the fixation of carbon dioxide, has been observed by Osterhout and Haas (5), and explained by them, "by assuming that sunlight decomposes a substance whose products catalyze photosynthesis or enter directly into the reaction."

It may be assumed that these reactions only take place when the leaf is exposed to light, and that their velocity under normal conditions is dependent on the intensity of illumination. The velocity of the first reaction would, however, be increased by increased illumination only so long as carbon dioxide is in excess, whereas the velocity of the second reaction would not be directly influenced by this factor. It is probable, therefore, that in strong sunlight the balance between the two reactions would be disturbed, tending to an increased proportion of chlorophyll *a*.

The following figures, deduced from the means of Willstätters' results (7), seem to bear out this view :—

Proportion of Chlorophyll a to Chlorophyll b.

Name of plant.	Sun leaves.	Shade leaves.
Sambucus nigra,	2·745	2·030
Aesculus hippocastanum,	2·687	2·268
Platanus acerifolia,	3·370	3·100
Fagus silvatica,	3·075	2·875

In the plant exposed to light in absence of carbon dioxide one would expect that chlorophyll *b* would be very much diminished in amount, if not altogether absent. This does not seem to have been tested by experiment.

The authors wish to express their indebtedness to Mr. T. G. Mason, M.A., B.SC., for some preliminary experimental work on the sensitization of gelatine photographic plates, and also to the Royal Dublin Society for supplies of liquid air, which made the experiments at low temperature possible.

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XXXIV.

THE BIONOMICS OF THE CONIDIA[1] OF *PHYTOPHTHORA INFESTANS* (MONT.) DE BARY.

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In previous papers (18, 19)[2] accounts were given of field experiments in Canada and in Ireland bearing on the occurrence of blight in potato tubers, particularly after digging. It was shown that the bulk of the infection in the case of potatoes which develop blight in storage is contracted when the tubers are being dug. Proof was given that contact of the tubers with partially blighted foliage results in serious rot in storage. Evidence was also presented to show that soil contaminated with conidia shed from the leaves continues capable of inducing blight in freshly dug tubers which are brought into contact with it for a period of at least ten days, and probably longer. It was mentioned that the part played by contaminated soil was fully established by the results of laboratory investigations. The present paper deals with this phase of the subject.

I.—Vitality of Conidia.

Vitality of conidia in soil out-of-doors.—As it is generally accepted, following de Bary (4), Jensen (11), Hecke (10), McAlpine (14), Jones, Giddings and Lutman (12), and Melhus (17), that the life of the conidia in comparatively dry air is measured in hours rather than days, an attempt was made to determine the effect of keeping the conidia in soil.[3] A preliminary

[1] The word "conidium" is used throughout to describe the asexual reproductive body which behaves sometimes as a conidium and sometimes as a zoosporangium.

[2] The numbers in brackets refer to the list of literature cited at the end of the paper.

[3] Jensen (11) found by experimental methods that conidia may survive in soil for five days. Apart from this experiment, no other reference to the subject has been found in the literature, with the exception of certain observations of de Bary (3) on the vitality of conidia in soil which had carried a blighted crop; of Melhus (16) on the behaviour of conidia produced on the surface of infected tubers in the soil; and of Peters, as reported by Karsten (13), on the continued vitality of infecting material placed on the soil. Although the matter was not followed up, the conclusions reached point in the same direction as our own results, particularly in the last two cases. See also Appel (1).

experiment indicated that by so doing the spores remained viable and capable of infecting potatoes for several days.

On September 15th the following experiment was begun. Finely sifted potting loam, in a comparatively dry condition, was dusted on the lower surface of potato leaves which carried a strong growth of conidiophores of *Phytophthora infestans*, and was then brushed off again with a fine brush. In this way a quantity of soil, weighing about 400 grams, was so copiously contaminated that it was easy to find conidia in any fraction when examined microscopically. The soil so prepared was divided into four parts, each of which was placed in the form of a little mound on the surface of similar loam which filled a flower pot. Four similar pots were prepared in which were placed like quantities of sifted potting loam which had not been contaminated. All the pots were placed on a roof exposed to the weather but shaded from the sun for part of the day. The length of time the conidia survived was determined by inoculating a little of the soil from the mounds into shallow wounds in healthy tubers.[1]

Using this method, it was found that the fungus remained capable of infecting tubers for twenty-one days, but not for twenty-eight days. The first inoculations on the unwounded surface were failures; thenceforth they were made in wounds, with the result that on the 13th day, 8 out of 8 inoculations were successful; on the 19th day, 4 out of 8; on the 20th day, 4 out of 6; on the 21st day, 3 out of 6; on the 28th day, 0 out of 8. Throughout the experiment no disease developed in any of the thirty-two wounds in which was placed soil similarly exposed but not contaminated with conidia.

This experiment was conducted during the driest portion of the year, from September 15th to October 6th, 1920. Notwithstanding their exposed position the conidia survived this. Torrential rain occurred on October 2nd

[1] Examinations were first made microscopically, but it was found that searching for viable conidia in soil, and then testing their germination, was a time-consuming operation. Reliance was, therefore, placed on infection experiments on potato tubers with adequate controls. At first whole tubers were used, the inoculum being introduced into wounds, while similar potatoes from the same lot were wounded but not inoculated. The bulk of the work, however, was carried out on potato slices, and a portion from every tuber used was left untreated. In all the critical experiments an "adjacent surface control" was allowed to every inoculated slice, that is, the two surfaces which were in contact before a tuber was cut were used as a check on each other, one being inoculated and the other not. It may be stated that of the 232 control pieces used throughout all the experiments to be described, only four failed to remain sound, and none developed blight. In no single case did non-contaminated soil produce blight, and it was always used for comparison with contaminated soil. In all the work, with the exception of some of the preliminary experiments (in which the typical appearance of blight rot was deemed sufficient), infection was not admitted until the parasite was recovered from the infected material.

and 3rd, but it was not until three days after this that the last successful infection was found.

Vitality of conidia in clay, sand and salts.—As the contaminated soil which was the first to fail to produce the disease in the last experiment was in a pot which had been taken indoors during the previous few days, the effect was tried of mixing conidia with a quick-drying medium, such as silver sand, in comparison with clay. As it had been claimed[1] that the conidia were capable of living over winter in a mixture of calcium sulphate and calcium carbonate, this medium was also tested. The clay, sand, and salts were kept in Petri dishes.

The results are shown in Table I. The clay mixture produced blight up to twenty-one days after being made up, the sand mixture up to seven days, and the salts (although they were perfectly dry throughout) up to twelve days. No disease developed from any of the forty-two control inoculations in which clay, sand and salts respectively were used.

TABLE I.—Length of life of conidia in clay, silver sand, and salts mixture in room.

	Successful infections after						
	3 days.	4 days.	5 days.	6 days.	7 days.	12 days.	21 days.
Clay, .	6/6	6/6	6/6	6/6	6/6	6/6	5/6
Sand, .	5/6	6/6	6/6	4/6	1/6	0/6	—
Salts, . .	6/6	6/6	6/6	6/6*	6/6	1/6	—
Controls,	0/6	0/6	0/6	0/6	0/6	0/6	0/6

(In the case of the numbers expressed as fractions, the denominator represents the number of inoculations and the numerator the number of infections secured.)

In this experiment the sand and clay were slightly moist, and as nearly uniformly so to begin with as possible. The sand became noticeably drier during the course of time, and to this fact, possibly, the early death of the fungus is to be attributed. On the other hand, the salts mixture was air-dry to begin with, and it was left in this condition. The surprising length of time which the fungus survived in it appears to be attributable to the fact

[1] Griffiths, Chemical News, vol. 53, 1886, p. 255. This experiment was repeated under the conditions given (in a dry incubator at 35° C.) but with an entirely different result from that claimed.

that the conidia became coated with the medium, a feature which is also found in examining contaminated clay.

Effect of moisture on the vitality of conidia in soil.—In order to determine the effect of excessive moisture and lack of moisture on conidia in the same kind of soil, three ordinary flower pots were filled with moderately dry potting loam. In the surface of the soil in each pot there was sunk a small paper cylinder, the diameter and depth of which were each about 2·5 cm., and the cylinders were then filled with loam as uniformly contaminated as possible with conidia from potato leaves. Four days afterwards, when the soil had settled, one pot was watered copiously with a fine rose until water ran freely from the bottom; another pot was soaked by standing it in water until the soil was absolutely saturated; the third was left unwatered. Thereafter, until the end of the experiment, no more water was added. The three pots were kept in a cool room, the central portions, including the paper cylinders, being covered with Petri dish lids. Throughout the greater part of the forty days of the experiment the pots maintained different degrees of moisture, the soaked pot being water-logged, and by far the wettest, the watered pot intermediate, and the unwatered pot driest. The contaminated soil was tested periodically by transferring portions of it to slices of potato tubers.

The result was, as may be seen from Table II, that the dry and moist soils reproduced the disease for forty days, while that in the water-logged pot did so (though rather irregularly towards the end) for twenty-six days. Beyond this period, in both cases, the result was uncertain, for while some rot followed after the later inoculations, the blight fungus was not recovered. This feature was noted rather regularly towards the end of several experiments. It may be that the small amount of *P. infestans* which remained viable set up a weak rot and was soon swamped by saprophytes; or perhaps, as has been noted several times, old and apparently dead mycelium and conidia have a toxic action on potato tissue, setting up small local lesions which sometimes provide a foothold for other micro-organisms. Thirty-six control inoculations, using similarly treated but non-contaminated soil, gave negative results. It is, therefore, clear that, contrary to the views accepted since the time of de Bary, *P. infestans* may remain capable of attacking potatoes in the soil, even when the latter is water-logged, for comparatively long periods. The most favourable conditions for survival are found under the more or less dry conditions reproduced in the "dry" and "moist" soils. At the close of the experiment there was little difference in the amount of moisture present in these two pots.

TABLE II.—Length of life of conidia in dry, moist and water-logged loam.

Days from beginning of experiment.	Successful infections.		
	Dry soil.	Moist soil.	Water-logged soil.
1	4/4	4/4	4/4
3	4/4	4/4	4/4
5	4/4	4/4	4/4
8	4/4	4/4	4/4
10	4/4	4/4	3/4
13	4/4	4/4	3/4
16	4/4	4/4	4/4
19	4/4	4/4	1/4
22	4/4	4/4	0/4
26	4/4	4/4	1/4
30	4/4	4/4	0/4
33	4/4	4/4	0/4
40	3/4	3/4	0/4

(In the case of the numbers expressed as fractions, the denominator represents the number of inoculations and the numerator the number of infections secured.)

Effect of temperature and moisture on the vitality of conidia in soil.—A further experiment was carried out with similarly contaminated loam which was kept in small glass sample-tubes tightly stopped with cotton-wool. These tubes were placed three together in larger tubes, also stopped with cotton-wool, and put standing mouths downwards. This procedure was intended to arrest drying up without unduly cutting off the air supply. The tubes were stored under various conditions, as shown in Table III. The soil was dry and friable to begin with. It was left in this condition in some cases, and in others was made moist without being saturated. At intervals of a few days inoculations were made on potato slices, with the following results :—

TABLE III.—Length of life of conidia in loam kept in glass tubes.

Nos. and places of storage.	Original condition of soil.	No. of days after which successful infections were made.											
		3	6	9	12	14	17	20	23	26	30	34	37	44
1. Out-of-doors, Nov. 6–Dec. 20,	Dry	4/4	4/4	4/4	—*	—	—	—	—	—	—	—	—	—
2. Do.,	Moist	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4
3. Unheated room,	Dry	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	0/4	0/4	0/4	—
4. Do.,	Moist	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	3/4	2/4	2/4	?	?
5. Heated room,	Dry	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	0/4	0/4	0/4	—	—
6. Do.,	Moist	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	2/4	1/4	2/4	—
7. Incubator at 20° C. Saturated atmosphere,	Dry	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4	4/4
8. Incubator at 25° C. Dry atmosphere,	Dry	4/4	4/4	4/4	0/4	0/4	0/4	0/4	0/4	—	—	—	—	—
9. Incubator at 30° C. Saturated atmosphere,	Dry	4/4	4/4	4/4	4/4	4/4	4/4	4/4	3/4	1/4	0/4	0/4	?	—
Soil and tuber controls,	—	0/12	0/12	0/12	—	—	—	—	—	—	—	—	—	—
Tuber controls,	—	—	—	—	0/4	0/2	0/3	0/4	0/4	0/4	0/4	0/4	0/4	0/4

* Tube lost.

(In the case of the numbers expressed as fractions, the denominator represents the number of inoculations and the numerator the number of infections secured.)

The longest period during which the fungus was definitely proved to have retained its vitality in soil was forty-four days. It is worthy of note that with two of the tubes (Nos. 2 and 7) infection was just as easy and certain after the lapse of this period as at the beginning. From the same two tubes infection of potato slices was again secured sparingly after sixty-six days, and a still further trace of infection was obtained from No. 2 after seventy-four days, but in none of these cases was *P. infestans* recovered. Pieces of tubers inoculated after the last two intervals from other tubes (sixteen in number) and with similar non-contaminated soil (eight in number) remained sound.

The conditions under which the fungus survives longest are evidently determined more by moisture than by temperature. The longest periods of activity were found in tubes which were either moist to begin with or were kept in a saturated atmosphere, irrespective of the temperature up to and including 20° C. At 30° C. the temperature becomes important in spite of the abundance of moisture. The most fatal conditions are those which combine high temperature and dry soil.

Attempts at direct examination of contaminated soil.—Direct examination of the soil failed to give an explanation of these findings. It was concluded, after careful search, that the fungus did not survive in the form of mycelium. On the other hand, apparently perfect conidia, among others, were still seen in soil to which they had been added more than three weeks previously. The majority of the conidia observed under such conditions appeared, however, to be shrunken but ungerminated. Others were empty, and from the presence of apical openings were concluded to have produced zoospores. No germ tubes were seen. Soil samples such as these, when placed on potato slices, infected them freely, while similar slices not inoculated remained sound, so that in the apparent absence of mycelium it was concluded that the conidia themselves had the power of retaining their vitality for comparatively long periods.

An attempt to prove this by placing fresh conidia on twelve dry cover glasses in a small chamber, the atmosphere of which was saturated with water-vapour, proved only partially successful. Twelve other cover glasses similarly provided with conidia and prepared at the same time were placed in a similar chamber which was kept dry. The period of life was tested by infecting potato slices (with controls) from the fifth day onwards. The conidia from the moist chamber produced disease regularly until the ninth day, but not afterwards. Neither the conidia from the dry chamber nor the controls produced disease on any day. A later experiment in which the moist chamber was closed with a water-seal led to no better result.

Notwithstanding these findings, based as they are on laboratory experiments, there are indications that the life of conidia in air may be longer under more natural conditions. When a vigorous growth of conidiophores is left undisturbed for some time, it is noticeable that the fringe of the growth contains conidia which are few in number and of poor germinative capacity. Further in towards the substratum numerous and more vigorous conidia may be found. It is probable that the air in the centre of such masses of mycelium is more moist than in the fringe, which would account, to some extent, for the result. At the same time the comparatively low vitality of conidia when removed from the conidiophores and kept in a saturated atmosphere would go to show that another factor besides moisture must be involved. It is possible that large masses of mycelium contain an abnormal proportion of carbon dioxide, arising from the hyphae themselves, the substratum, or from bacteria and other contaminations, and that this has an influence on the conidia. The bearing of a reduced oxygen supply on the germination and vitality of the fungus is discussed more fully in later paragraphs.

The view sometimes expressed (3, pp. 38 and 39; 4), however, that that the conidia may live for some weeks in dry air under certain conditions, while in moist soil their existence is shorter owing to germination supervening after the first rain, is in opposition to our results.

An experiment was twice repeated in which columns of sifted loam and silver sand, each 10 cm. deep, were contained in two upright glass tubes, each having a diameter of 2·8 cm. The tubes were open at the top, and had an arrangement to permit of drainage water escaping at the bottom. After the materials in the tubes had settled, a small quantity of contaminated sand was placed on the surface of the loam and sand. Water in measured quantities was then allowed to drip at fixed rates on the contaminated soil in the tubes. The liquid which came through at the bottom was caught on filter papers, which were transferred at regular intervals to the cut surfaces of potato tubers. The experiments were continued for six and five days respectively.

It was found in these experiments that the filter papers became sparingly pathogenic to potato tubers after the passage of water equivalent to a "rainfall" of 40 to 80 cm. or more, and seventeen to forty-one hours after the "rain" began. In the first experiment the sand alone allowed the infecting material to pass through, this occurring after twenty-six and a half hours, and none coming through the loam. In the second test (begun twelve days after the commencement of the first, the same tubes and soils being used as before, but with the addition of fresh contaminated sand) infecting material passed through the loam filter only, and that after seventeen, twenty-four

and forty-one hours. In the light of later experience, the possibility that this material was left in the loam from the previous experiment must not be overlooked. The most significant point was that in three cases out of four in both experiments the originally contaminated surface-soil was more pathogenic to potatoes, even after a period of three to three and a half days, during which water equivalent to 162 cm. (approximately) of "rain" had passed through it, than the drainage water was at any time. The longest period of pathogenicity of the surface-soil under the conditions of continuous "rain" slightly exceeded four and a half days.

II.—Germination of Conidia.

Previous work on the germination of the conidia.—It was conceived that the method by which the conidia germinated might have a bearing on the period of vitality, zoospores being probably more delicate than germ tubes. It was found difficult, however, to deduce from previous work which method might be expected from conidia in the soil.

While Berkeley and Montagne (6) saw the early stages of zoospore formation within the sporangium, and de Payen (20) observed the emptying of the latter, the meaning of the process was unknown to them and to the earlier workers, such as Morren in 1845 (according to Hecke), Schacht (22) and Speerschneider (24), all of whom observed direct germination.[1] It was not until 1860 that the production of zoospores was recorded by de Bary (2) for *P. infestans*. De Bary (3, 4) was not able to find exactly what the conditions determining the two methods of germination were. He was first of the opinion that germ tubes were formed only when the tubers were infected in the ground, but later found that this did not always hold. He regarded zoospore formation as the normal procedure, and suggested that germ tubes were produced only by old conidia of low germinative power. Strong sunlight prevented the formation of zoospores. A third method of germination described by this author (2, 3, 4) for the first time consisted of tube formation followed at once by the production of a secondary conidium. De Bary regarded this as a specific mode of germination, due to partial immersion in water. The secondary conidium had the power of producing zoospores, or a tertiary conidium might result.

Marshall Ward (25), to whom we owe the fullest and most accurate description of the germination process, considered that zoospore formation was favoured by the presence of oxygen in the water and by the absence of

[1] That is, the production of germ tubes. When zoospores result, the germination is said to be indirect.

organic matter, such as jam or dung, and of too strong sunlight. Tube germination followed by the formation of secondary conidia, while depending to some extent on the conidia themselves, was favoured by light, thick sowing, and by any cause which delayed germination. A temperature factor did not seem to be involved.

Hallier (9) found that zoospores were formed only when food was lacking, while germ tubes resulted in nutrient solutions. Smorawski (23) apparently arrived at the same result. This conclusion Hecke (10) also largely supports; but in so far as he found no zoospores produced in solutions containing more than 0·5 per cent. of dry matter, while germ tubes occurred not only in such solutions but were sometimes associated with zoospores in very large numbers in distilled water, he concluded that some peculiarity must lie in the conidia themselves. His conclusion was that very young conidia only ("eben erst gebildete Konidien") can produce zoospores, but that they do so imperfectly (with partial extrusion of the contents) in nutrient solutions. Older conidia never form zoospores. Their germination is poor in distilled water and generally closes with a secondary conidium, while in nutrient solutions they germinate well.

Brefeld's (8) conclusion with regard to zoospore production in the Peronosporaceae (including *P. infestans*) was that thorough wetting favoured this form of germination.

McAlpine (14) found that the first crop of conidia produced zoospores, while the later crops were variable. A short period of drying prevented zoospore formation.

Jones, Giddings and Lutman (12) found that potato juice favoured direct germination and that temperature also affected the process. "At 25° C. more than 50 per cent. of the germinations are by tubes, . . . while at 10° to 20° C. direct germination is exceptional."

According to Melhus (17) the determining factor does not consist of age or any innate peculiarity of the conidia; nor of light, the concentration of the solution, or the amount of oxygen available. On the other hand, temperature is all-important. At 13° C. the maximum of zoospore formation is found, while at about 23° C. this has practically ceased and germ tubes are the rule. It is only in extremely strong nutrient solutions (20 per cent. dextrose) that zoospore formation is replaced by some direct germination.

Fresh experiments on the germination of the conidia.—The results of previous work on the conditions regulating the manner of germination being found so conflicting that no conclusion could be drawn, the problem had to be taken up afresh. Fortunately in the course of this investigation it was

found possible to reproduce conditions in microscopical preparations under which the conidia remained viable and capable of infecting tubers for several weeks. As these conditions resemble in many respects those which occur in soil, it is reasonable to suppose that the explanations which will be given of the phenomena observed in the preparations are also applicable to natural conditions.

This portion of the work also resulted in extending our knowledge of the morphology and biology of the fungus in some important particulars, one of which at least has a bearing on the fate of conidia in the soil.

The findings of Hecke and Melhus were first compared. For this purpose the germination of conidia was tested in the following liquids, which were sterilized before using:—(1) distilled water, (2) tap water, (3) soil extract, prepared by the slow filtration of tap water through four inches of soil, and (4) a 1·5 per cent. solution of glucose in distilled water. To observe the effect of temperature, one set of germination tests in these media was carried out at room temperature (which during these trials never sank below 10° C. at night, or rose above 15° C. during the day, with one exception, when 22° C. was reached), while another set was carried out in a constant temperature incubator at 22°–23° C. Both sets were kept in the dark. Conidia were derived from Petri dish cultures on potato slices, which were infected from pure cultures on oat agar. Every care was taken to use uniform material from the same culture for both sets of tests. The germinations were carried out under cover glasses (except in some special cases), and the slides were kept in moist chambers to prevent drying. It is possible in this way to keep the same preparation under observation for several weeks, and to change the liquid at will without materially disturbing the conidia.

Comparison of the effects of nutrient solutions and temperature on germination.—Our work on the conditions (so far as they were tested) governing the germination of the conidia agrees best with that of Marshall Ward (25). These conditions were found to be very complicated, as would be expected from the results of earlier investigations. The comparison of the effect of the solution and of the temperature was repeated seven times without achieving a constant result, as may be seen in Table IV.

TABLE IV.—Influence of nutrient solutions and of temperature on the germination of conidia.

Date of Experiment.	Distilled water.		Tap water.		Soil extract.		Glucose 1·5 per cent. sol.	
	Germination.	Method.	Germination.	Method.	Germination.	Method.	Germination.	Method.
10°–15° C.								
23. 2. 21	Good	S only	None	—	Good	C (24) S (16)	Good	S (25) C (4)
24. 2. 21	Poor	S ,,	Good	S only	Poor	S only	Good	S only
25. 2. 21	Fair	S ,,	Poor	S ,,	Fair	S ,,	Poor	S ,,
26. 2. 21	Good	S (122) C (2)	Fair	S (20) C (4)	Good	S (91) C (11)	Good	S ,,
28. 2. 21	Good	S only	Good	S only	Good	S (99) C (22)	Good	S ,,
1. 3. 21	Good	S (*n*) C (1)	Good	S ,,	Good	S only	Good	S ,,
2. 3. 21	Good	S (*n*) C (1)	Good	S (*n*) C (1)	Good	S (*n*) C (1)	Fair	S ,,
22°–23° C.								
23. 2. 21	Fair	C only	None	—	Fair	C only	Poor	C only
24. 2. 21	Trace	C ,,	Poor	C only	Good	C ,,	Trace	C ,,
25. 2. 21	Trace	C ,,	Poor	C ,,	Good	C ,,	Trace	C ,,
26. 2. 21	Fair	C ,,	Fair	C ,,	Poor	C ,,	Trace	C ,,
28. 2. 21	Trace	C ,,	Trace	C ,,	Fair	C ,,	None	—
1. 3. 21	Fair	S ,,	Good	S (56) C (17)	Trace	C ,,	Good	S only
2. 3. 21	Fair	C ,,	Trace	C only	Trace	C ,,	Fair	C ,,

S stands for spores functioning as sporangia; C for those functioning as conidia. The figures following in some cases represent the relative numbers counted. The symbol (*n*) represents a very large number.

The following conclusions from this experiment seem to be justified (see Table IV):—

Temperature of 10°–15° *C.*

1. At a temperature of 10°–15° C. the regular method of germination is by means of zoospores. With good material the germination runs from 50 to nearly 100 per cent.

2. Generally speaking, the number of conidia producing germ tubes at this temperature is small, but it may under certain conditions exceed the number producing zoospores.

3. The influence of nutrient solutions on the production of germ tubes was not apparent in the case of the sugar solution used, but there was, perhaps, somewhat more evidence for it in the case of soil extract. A somewhat larger number of abortive (unescaped) zoospores was found in the sugar and soil solutions than elsewhere.

4. There is considerable evidence that the tendency to produce germ tubes at a temperature of 10°–15° C. rests in the conidia themselves (see test of 26. 2. 21 at 10°–15° C.).

Temperature of 22°–23° *C.*

1. At 22°–23° C. the regular method of germination is by means of germ tubes. The germination seldom exceeds 50 per cent., and is generally less.

2. Ordinarily the production of zoospores is rare, but conidia with undifferentiated contents but with the papilla gone, or with contents extruded, or containing abortive zoospores, are frequent.

3. On one occasion (test of 1. 3. 21 at 22°–23° C.) the production of zoospores largely replaced that of germ tubes, indicating either a peculiarity on the part of the conidia then used, or that temperature does not act directly on germination, but influences it through some factor which it generally (but not always) calls into play.

4. The influence of nutrient solutions was not marked, but soil extract seemed to favour tube formation.

The tests carried out at 22°–23° C. gave percentages of germination which were uniformly much lower than those found at the lower temperature. It was evident that the conidia were near the limits of their development. It is believed that the results recorded have little, if any, bearing on the conditions under which blight epidemics occur.

Effect of age on the method of germination.—Some conidia germinate by means of germ tubes under conditions which cannot be explained by reference

to aëration, presence of other organisms, temperature or nutrient solutions. From a consideration of the frequently different behaviour of two conidia lying close together under apparently similar conditions, one is forced, along with most previous workers, to conclude that different potentialities must reside in the bodies themselves. This was one of de Bary's views, and his suggestion that germ tubes are the result of age and lack of vigour has been endorsed by many of his successors without any convincing proof being adduced to support it.

Evidence in support of this view can, however, now be given. Conidia were tested from an eight-months'-old pure culture on oat agar. The aërial portion of the mycelium at least appeared dead, and it must have been a considerable time since any conidia had been produced. There were, however, some perfect conidia present among a multitude of dead ones. The former germinated in sterile water at 10°–15° C., somewhat slowly but strongly, and entirely by means of germ tubes. A peculiar feature of their germination was that the tube or tubes (often up to five) occasionally sprang from all parts of the wall, although generally they came from the normal place beside the papilla. These conidia were also peculiar in possessing a yellowish oil drop and an unusually prominent papilla, just like secondary conidia. It is conceivable that this is the outward sign of their having gone through some maturation process.

Similarly with conidia placed in water, whether primary or secondary, if they do not germinate within about twenty-four hours they seem practically incapable of producing zoospores. Here again in most cases (always, indeed, with secondary conidia) we get the same signs of an inward change. Furthermore, when such conidia lie long in water (three weeks), the germ tube may arise from any part of the wall.

An attempt, however, to distinguish between conidia from a comparatively fresh growth which germinate by means of tubes soon after being placed in water at 10°–15° C., and those with a similar origin which produce zoospores, resulted in failure. Many conidia apparently similar in all respects were marked, some of which afterwards germinated in one way and some in the other. It was observed that only the hyaline conidia germinated at all. Those which were at all dark-coloured or slightly plasmolysed failed to grow.

III.—Effect of Lack of Oxygen on Development of Conidia.

Germination delayed or prevented by lack of oxygen.—During the course of these tests it was noted several times that the presence of bacteria or yeasts

arrested germination. It soon became possible to distinguish between conidia which were incapable of development and those the development of which was merely delayed. The least sign of plasmolysis is a sure index of death, but before this appears a peculiar darkening and granulation of the protoplasm indicate, according to our experience, that the conidium is incapable of development.

It was found that some slides (particularly those kept at 23° C.) became badly contaminated with bacteria and yeasts, and that under such conditions germination was confined to a zone about 4 mm. wide near the edge of the cover glass. Within this ring a negligible amount of germination, or none whatever, was to be seen. If, however, the slide was very carefully and repeatedly irrigated with its appropriate solution, the process being watched under the microscope and extreme caution being exercised not to disturb the conidia, it was found that the germination of a large number of the central conidia could be brought about. Three hours after irrigation the result was sometimes apparent, but sometimes it took twenty-four hours. While traces of indirect germination have been seen under these circumstances, germ tubes are almost the invariable rule, irrespective of the temperature or of the nature of the solution.

This experience was repeated many times, at first involuntarily and afterwards of set purpose. A test in tap water at 23° C., begun on 2. 3. 21, became contaminated with bacteria after twenty-four hours, and then showed only 18 conidia with germ tubes out of 198 conidia examined. Most of these were near the edge, there being very few in the centre. After irrigation and a further period of twenty-four hours, the number of conidia with germ tubes was 112 out of 271 examined. Another slide containing soil-extract and belonging to the same series also became contaminated and showed four conidia with germ tubes out of a large number examined after twenty-four hours. On irrigation the number rose to 34 in 89.

That it was the presence of bacteria which prevented germination was proved repeatedly by setting up some tests under practically sterile conditions, while in others bacteria were introduced. The former (at 10°–15° C.) showed numberless zoospores after about three hours, and after twenty-four hours the majority of the conidia had germinated in this way all over the slide. Where bacteria had been introduced perfect zoospore formation was found only in a narrow zone near the edge of the cover glass, while there might be attempts at zoospore production elsewhere. If now fresh water were copiously introduced a great access of germination resulted in most cases, germ tubes only being produced. Control slides to which no water was added showed no change, or at most an entirely negligible amount of tube

production. Corresponding results were secured with preparations kept at 22°–23° C.

This experiment was repeated using motile protozoa along with conidia, which makes a beautiful preparation. The protozoa after twenty-four hours are confined to a narrow zone near the edge of the cover glass, in which they swim about freely. In this area, and extending somewhat within it, good germination is to be found, whilst still further in there may be no germination whatever. Motile bacteria exhibit the same zonation to some extent, the outer ones only being in motion. Penicillium spores have also been used with somewhat similar results. In this case the rapid development of *P. infestans* allows some zoospores to be produced, but a great many become abortive.

These results, it is believed, are to be explained by the fact that the competing organisms use up the oxygen in the water and replace it with carbon dioxide faster than the conidia can utilize it for the purpose of germinating. There may be a question of other excretion products having an inhibitory effect, but judging from the variety of organisms used this is hardly likely. The same effect has been produced by sealing round the edge of the cover glass with melted paraffin. Furthermore, the conidia themselves, if the slide is very thickly seeded, bring about the same result. When germination is general around the outside of a clump, there is often none at all in the centre. Conidia scattered among the hyphae of living mycelium of *P. infestans* frequently behave similarly.

Formation of secondary conidia.—Secondary conidia, as originally described by de Bary (2, 3, 4), are the immediate products of previously existing conidia, being borne on the germ tubes of the latter. The name "secondary conidia" is not a particularly good one, for conidia morphologically and physiologically identical are produced by hyphae which fructify in water, and identical but smaller bodies may be formed by zoospores, as will be shown. The term is used in a somewhat loose sense in this paper for the new conidia which sometimes follow after the germination both of conidia and of zoospores. Such secondary conidia seem to owe the characteristic appearance which is common to them and to conidia produced by submerged hyphae to the fact that they are formed in water, on which account a word like "hydro-conidia," which would include all three, might be preferable.

The conditions under which germination is arrested but subsequently takes place are favourable for the production of secondary conidia. These have been very common on our slides. When germ tubes are formed in the presence of bacteria, or when bacteria are introduced after their formation, secondary conidia will always be met with within a zone from about 2 to 4 mm.

wide inside the edge of the cover glass. In preparations sealed with paraffin they are found only at the extreme edge. Their formation is constant, and is the result of specific conditions. At a certain degree of oxygen concentration which just permits germination, or when the oxygen supply is gradually cut off after germination has taken place, secondary conidia are produced. Bacteria are the most reliable agents for bringing about this state of affairs, as may be seen by introducing them into one of two uniform preparations. At a still lower oxygen concentration ungerminated conidia are eventually (and sometimes rapidly) killed; but there is evidence derived from sealed preparations to show that germ tubes continue living for several weeks, and even increase in length, with a still scantier oxygen supply. This is possibly connected with the greater amount of exposed surface, which facilitates respiration. For some reason which has not been established, secondary conidia appear to be materially more resistant than are conidia formed in air to the adverse influences they meet with in water in competition with other organisms; and they are, therefore, an important adaptation to certain aquatic conditions.

The formation of secondary conidia has been mentioned by most workers since their discovery by de Bary (2, 3, 4), but certain new observations may be recorded. The conidia which give rise to them rapidly lose all their contents, which pass in their entirety into the smaller and less symmetrical secondary bodies. If the primary conidium has two germ tubes a secondary conidium may be produced by each. The hypha joining the primary and secondary conidia is of variable length, or may exceptionally be lacking, the second conidium being an asymmetrical prolongation of the first. The germ tubes generally grow in the direction of the greater oxygen concentration. Frequently the new conidia are found in the free water surrounding the cover glass, being borne on very long tubes springing from conidia lying further in. These hyphae grow straight to the margin, perhaps after a preliminary turn. The secondary conidia have thinner walls and more rounded and prominent papillae than the original ones, and they always contain one (or occasionally two) yellowish oil-drops. Even when lying in the free water around the cover glass they may remain ungerminated but viable for about three weeks. Frequently, however, they germinate sooner, and they may produce zoospores if the conditions are favourable; but germ tubes are the general rule, frequently followed by a third conidium, as de Bary and others have described. These have frequently been seen, and on several occasions even what may be called a quaternary conidium, four conidia in a chain, each somewhat smaller than the preceding one. It is conceivable that repeated germination and conidium formation may result in

a further lease of life, analogous to the survival of mycelium under circumstances which are fatal to fresh conidia.

Zoospores and the production of "secondary" conidia.—When conidia germinate by the production of zoospores, the latter, in the presence of sufficient oxygen, settle down after a longer or shorter period of activity, develop a cell wall and immediately put out a germ tube. There is no doubt that oxygen in sufficient quantity favours this whole proceeding. When oxygen is lacking the germination is often abortive, even at favourable temperatures. The zoospores may be more or less differentiated, but none may emerge; or some or all may escape, but they do not swim far from the sporangium and soon come to rest. Under such conditions it frequently happens that no cell wall is formed, and the zoospore dies and dissolves. That it is lack of oxygen which limits the activity of the spore in these respects is shown by the presence of naked and otherwise abortive zoospores among masses of Phytophthora mycelium. The coming to rest of large numbers of zoospores in a cluster, which is sometimes seen under these conditions, is explainable on similar grounds. The chance coming of one or more into a zone of low oxygen concentration puts an end to their activity, and the accentuation of the dearth of oxygen which their presence causes entraps other zoospores which happen to swim into the locality, and so the process goes on.

When the zoospores germinate under favourable conditions, the germ tube is of such enormously greater capacity than the original spore, and continues increasing in length (even though not completely filled with protoplasm), or at least remains alive and vigorous-looking so long, that a saprophytic existence is at once suggested (7). However this may be, it is certain that the zoospore germ tubes can live for one week in water, for they have been directly observed to do so for that period. The statement of de Bary (3) that they cannot live longer than twenty-four hours under such conditions is not correct. A single week, however, is not the limit of their existence. They, too, have the faculty of producing "secondary" conidia, an observation which does not seem to have been recorded previously. The conditions are the same as for conidium production by conidia—namely, a reduction in the amount of oxygen. The phenomenon was first observed in a sealed preparation where conidia had discharged zoospores surrounding an air bubble. Six days afterwards there was an attempt at conidium formation by a zoospore germ tube, but it did not come to fruition. Subsequently in a preparation originally set up under sterile conditions and kept for five days at 10°–15°C., in which there had been abundant zoospore formation, the

almost universal production of "secondary" conidia by the zoospores situated near the edge of the cover glass was observed. The slide had become contaminated with bacteria. These new conidia were borne on the ends of long spirally twisted germ tubes. They contained all the protoplasm, even of the branches, where such were present. In form they exactly resembled those produced by conidia, being asymmetrical, and provided with prominent papillae and yellow oil-drops, but they were much smaller, although having a considerably greater volume than the original zoospore. In a companion preparation, which was not contaminated, the zoospores did not produce "secondary" conidia.

It is evident that the faculty by which germinating zoospores may prolong their existence under unfavourable conditions by developing directly into conidia must be of significance in the life-history of the fungus. The general and rapid production of zoospores by conidia at relatively low temperatures and in subdued light is evidently an adaptation to facilitate leaf infection during the heavy night dews of late summer and autumn. It is probable that under these conditions failure to bring about infection in the night or morning hours results in the death of the spores, at least in dry weather. In the case of conidia which fall to the ground, even though they function as sporangia, it is clear, in the light of our present knowledge, that the resulting zoospores are not nearly so delicate as to lose their vitality (unless they succeed in infecting a potato tuber) a short time after the first shower of rain which brings about their liberation. The conidia produced by zoospores have probably a measure of the same power of resistance as is possessed by other secondary conidia, so that instead of a single body capable of living for days or weeks and then infecting the plant under favourable conditions, the eventual sources of infection are multiplied manifold. The extent to which this multiplication can go was not determined, but "secondary" conidia, the product of zoospores, were seen which were empty and open at the apex as though they, in turn, had again produced swarm spores.

Relation of results obtained in microscopical preparations to soil conditions.— The germination of secondary conidia was observed twenty-four days after the original conidia were placed in water, and the germ tubes of the former were still living after thirty-four days. Potatoes were infected many times with conidia which had been fifteen to sixteen days in water (during which time they had germinated, and in some cases produced further conidia), the entry of the germ tubes into thin slices of tubers being observed under the microscope. The hyphae grew between the cells, and fine convoluted branches were sent into the cells and between the starch grains. Where secondary conidia were not formed, the germ tubes were found to be an

important aid in prolonging life. While original ungerminated conidia produced in air were not observed to be viable after a period of five to seven days in water, germ tubes and secondary conidia are much more resistant.

The low oxygen concentration in which the slow development and continued vitality of the fungus were directly observed for comparatively long periods in microscopical preparations is believed to offer an explanation of the similar resistance exhibited in the soil. It is reasonable to suppose that all the conditions reproduced artificially must be realized in the soil, as well probably as many others.

According to Russell and Appleyard (21), there are two distinct atmospheres in the soil—the "free air" and the "dissolved air." The former does not differ in principle from atmospheric air, but it contains a larger and fluctuating amount of carbon dioxide (about 0·25 per cent.), and is almost saturated with water vapour. The dissolved air contains practically no oxygen, and is made up of carbon dioxide and nitrogen in varying proportions. It is shown that the oxygen requirements of the soil are always in excess of the supply, and thus the two bodies of air, though existing in close relationship to each other, retain their individual characteristics. Temperature, cultivation, manuring, and rainfall in particular, however, affect the soil atmospheres. A heavy fall of rain, which is nearly saturated with oxygen, partially renews the dissolved air. This, as evidenced by the subsequent rise in the CO_2 content, allows the development of aërobic organisms. Among the latter the conidia of *P. infestans* must find in the fluctuations of the dissolved atmosphere the conditions which enable them to survive for the long periods noted in the experiments with contaminated soil, and to germinate when conditions are made more favourable by the accession of water rich in oxygen.

There is another feature in the fluctuation in the amount of carbon dioxide in the soil which may influence the course of the blight fungus. The channel along which the parasite makes its way from the tubers to the leaves in spring is not known with sufficient certainty. The stem of the potato has been proved in a few cases to be penetrable by the mycelium, but the possibility of the transference taking place through the soil has hardly been studied. This is the more curious since the downward course of the parasite in the autumn from the leaves to the tubers is admittedly through the soil. It may be significant that the time at which the parasite finds its way downwards coincides with the minimum CO_2 content of the "free" soil atmosphere, while in the spring, when the course is upwards, the CO_2 content is at its maximum. The results of an experiment to test the capacity of the blight fungus to penetrate the soil were so suggestive that further attention is being devoted to the subject.

Summary.

The conidia of *Phytophthora infestans* when mingled with soil and kept out of doors may remain viable and capable of infecting potato tubers for a period of between three and four weeks.

The vitality of the conidia is retained longer in loam than in a quick-drying medium like silver sand.

In experiments indoors conidia survive longer in comparatively dry to somewhat moist soil than in very wet soil, the respective periods being forty and twenty-six days.

Temperatures up to and including 20° C. have no ill effect on the conidia as long as sufficient moisture is present. At 30° C. the temperature is not too high for the conidia to survive for twenty-six days if the atmosphere is saturated. The most fatal conditions are those which combine lack of moisture and high temperature.

Under the most favourable conditions indoors, conidia in soil infected tubers just as freely after forty-four days as when fresh.

Conidia when placed in soil survive without the production of obvious mycelium. The attempt to preserve ungerminated conidia in air saturated with water-vapour met with comparative failure, nine days being the apparent limit of existence.

Initially contaminated surface soil, after the continuous passage through it of large quantities of water, may remain pathogenic to potatoes for a period exceeding four and a half days, and generally infects potatoes more freely than the water after passing through 10 cm. of soil does at any time during the period.

As having a possible bearing on the resistance of conidia in soil, their method of germination was re-examined in the light of previous work, which is summarized.

At a temperature of 10°–15° C. the conidia germinate freely, and generally produce zoospores. A small number of germ tubes may, and often do, result; while exceptionally they may be in the majority. Nutrient solutions, such as soil filtrate and 1·5 per cent. glucose in water, are without material influence in favouring tube production; but such solutions hinder somewhat the perfect formation of zoospores. Abundant oxygen and the absence of competing organisms favour zoospore production.

The tendency to produce germ tubes at low temperatures seems to be innate in the conidia themselves. Conidia which have remained for some time ungerminated in air and those which have had their germination in water delayed for any reason seem capable only of giving rise to germ tubes.

At a temperature of 22°–23° C. the limit of development of the conidia is approached. The germination is comparatively poor and germ tubes are the general rule. While abortive sporangia are frequent, the production of perfect zoospores is rare. Exceptionally, zoospores may largely take the place of germ tubes. The reason for this is obscure, but is believed to lie in the conidia themselves.

Secondary conidia and old but still viable conidia from air resemble each other in possessing a more prominent papilla than usual, and a large yellowish oil-drop. These appear to be signs of their having undergone some maturation process which increases their resistance. Both as a rule produce germ tubes, generally more than one, which may spring from any part of the wall.

The germination of conidia in water is delayed by lack of oxygen, and may subsequently be brought about by the timely supplying of fresh water. Suspension of germination has been effected by means of bacteria, protozoa, Penicillium spores, thick seeding of conidia, and by ringing cover glasses with paraffin; and a good measure of germination has thereafter been effected by adding fresh water.

Secondary conidia, so called, are constantly produced at a certain degree of oxygen concentration which just permits germination, or when the oxygen supply is cut off after germination has taken place. In microscopical preparations they are confined to a zone near the edge of the cover glass, within which germ tubes may live and grow without having the power of forming new conidia. Ungerminated conidia from air are rapidly killed under the latter conditions.

Secondary conidia appear to be conidia adapted to an aquatic existence, similar bodies being produced by hyphae which fructify in water. They are more resistant than primary conidia, and this resistance is increased by the faculty they possess of successive germination followed by fresh conidium formation, which may be repeated four times. They may also produce zoospores under favourable conditions.

Zoospore germ tubes may also develop at once into "secondary" conidia when the oxygen supply is reduced after germination has taken place. Zoospore germ tubes may live for at least seven days in water, and their life is further lengthened when new conidia result. The secondary bodies so formed may apparently again produce zoospores.

The limit of existence of fresh ungerminated conidia in competition with other organisms in water is about five to seven days, and the period may be much shorter. After a germ tube is produced the resistance of the fungus is increased. Potato tubers have frequently been infected with such conidia fifteen to sixteen days after being placed in water. The germination of

secondary conidia has been observed twenty-four days after the original conidium was placed in water, and the resulting germ tubes lived at least ten days longer.

The conditions under which the continued existence of conidia, zoospores and germ tubes in water was directly observed for periods exceeding, in some cases, thirty days are believed to represent the conditions under which existence is possible for comparatively long periods in the soil.

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XXXV.

ON THE DISTRIBUTION OF ACTIVITY IN RADIUM THERAPY UNDER DIFFERENT CONDITIONS OF SCREENING.

By H. H. POOLE, M.A., Sc.D.,
Chief Scientific Officer, Royal Dublin Society.

[Read January 24. Published April 13, 1922.]

Introduction.

A great deal of work has been done by various experimenters on the passage of α, β, and γ rays from radioactive substances through various kinds of matter, and on the secondary radiations set up.[1] Some of the results so obtained are rather inaccessible to medical workers in this country, and, moreover, their application to specific problems is generally rendered difficult by the complexity of the radiations, and by the necessity of combining the effect of absorption with the geometrical effect of distance.

An attempt has accordingly been made to reduce the user's problem to its simplest form by carrying out tests on the screening effects of various materials for the combined β and γ radiation emitted by an emanation tube at a fixed distance, and combining the results so obtained with the geometrical law of distance, so as to calculate the variation of activity with distance from the source in some typical cases.[2]

It seems probable that we may take the ionisation produced in the tissues as a measure of the physiological action. This ionisation may be due to:—(1) α rays, (2) primary β rays, (3) secondary β rays produced by

[1] For a review of recent work on the absorption of γ rays see "Radium," October, 1921.

[2] The validity of this method has been questioned by Kroenig and Freidrich ["Strahlentherapie," xi, p. 20, 1920]. Their direct measurements of γ radiation at a depth of 10 cms. in water gave results about twice as great as they obtained by calculation. They attributed the discrepancy to scattered radiation. On the other hand, Sievert ["Acta Radiologica," i, p. 89, 1921] obtained results at smaller depths according excellently with theory. It would seem unlikely that, under the conditions prevalent in radium therapy, scattered radiation could cause a large error for distances up to 10 cms.

the action of the γ rays on any screen used, and (4) secondary β rays produced in the tissues by the passage of the γ rays.

The α rays are completely stopped by less than 0·1 mm. of flesh, or about 0·03 mm. of glass. This being much less than the usual thickness of wall of an emanation tube, they produce no effect with the common modes of treatment. If, however, emanation solution be injected, the effect of the α rays must far outweigh that of the others in all regions to which the solution finds access, as their relatively large energy and great absorbability cause, within their range, an intensity of ionisation about 100 times that due to the β rays.

The primary β rays, as may be inferred from the curves shown in fig. 2, are completely absorbed by about 1·5 cms. of flesh, or 1·5 mm. of brass. Owing to this comparatively rapid absorption, they produce relatively intense ionisation, that due to unscreened β rays being about 100 times that due indirectly to the γ rays from the same source.

Secondary β rays, produced by the passage of γ rays through ordinary matter, are similar in ionising properties to the primary β rays emitted by the radioactive source. They are, however, considerably less penetrating than the hardest of the primary β rays. The velocity, and hence the penetrating power of secondary β rays, increases with the hardness of the γ radiation to which they are due, so that the secondary β rays produced by γ rays are much more penetrating than those due to X rays.

If a metal screen is interposed between the source and the flesh, the surface of the latter is exposed to the secondary β radiation from the screen, but is deficient in secondary radiation from the flesh as compared with a point deeper down.

The effect at a point in the tissue, then, varies with depth owing to the combined effect of the following causes:—

(1) Absorption of primary β rays in the screen and the tissue.

(2) Absorption of secondary β rays due to the screen.

(3) Initial increase with depth of the secondary β rays due to the tissue.

(4) Absorption of γ rays, and consequent reduction of secondary β rays.

(5) Geometrical effect of distance.

The joint result of effects (1) to (4) has been estimated by experiments with an electroscope at a fixed distance from the source, and approximate calculations then made to include the effect of distance in some typical cases.

Apparatus.

The electroscope used is shown in section in fig. 1, which also shows the emanation tube mounted on a wooden block at a fixed distance below

the electroscope. It is made of brass, with a lead base 4 mm. thick, in the centre of which is a circular window, 2·7 cms. in diameter, covered with a sheet of gelatine, 0·02 mm. thick, off an unexposed but "fixed" photographic plate. The electroscope is lined with leather about 2·5 mm. thick, impregnated with gelatine containing a little mercuric chloride to increase its electrical conductivity. This lining ensures that the secondary radiation from the walls of the electroscope resembles as nearly as possible that in animal tissue, so that the rate of motion of the gold leaf is a fair measure of the total ionisation that would occur in the tissue under the same conditions of radiation. The electroscope was always charged to about 250 volts by means of a Tucker hygroscopic battery before each test. The approximate constancy of the initial voltage rendered the motion of the leaf more regular.

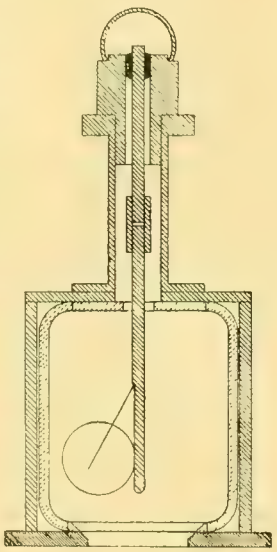

Fig. 1.

The screens to be tested were attached with a little plasticine to the under side of the lead base, the wooden block carrying the radioactive source being so arranged that it could be removed and replaced in the same position. This source consisted of one or more thin glass tubes about 1·5 cm. long by 0·8 mm. diameter, containing emanation, placed in a shallow groove in the block. The activity of the source used varied with the thickness of the screen so as to maintain the rate of motion of the gold leaf within reasonable limits. The screens were placed directly in contact with the electroscope base in order that as large a percentage as possible of the secondary β radiation, emerging at various angles from the upper surface of the screen, should enter the electroscope. The source was placed only 1·85 cms. below the base in order that the divergence of the γ rays passing through the parts of the base surrounding the window might reduce the error due to these rays to a negligible quantity. An allowance was made for the gelatine film in estimating the thickness of the various screens. Experiments with a second film indicated that the absorption of unscreened radiation by such a film amounted to about 6 per cent., so this allowance was made in estimating the effect of a bare emanation tube. In all cases the thickness of the screens used was found by weight.

Secondary Radiation.

The secondary radiation from various substances was compared by the usual method of using a compound screen of two or more materials thick enough to stop all the primary β rays, and observing how the ionisation current varied with the material which was next the window. It is of course necessary that the individual screens should be thick enough to emit their full secondary radiation. In this way the combined effect due to both γ rays and secondary β rays from the screen is directly measured. No appreciable difference could be detected between copper, zinc, brass, iron, tin, or silver. Taking the ionisation current due to γ rays and secondary β rays from any of these screens as 100, that with an aluminium screen was 105, with leather 3 mm. thick 110, and with lead 112. These results are in accord with those of previous investigators, who have found that the "emergence" secondary radiation is a minimum for an atomic weight of about 80.[1] They show that it is best to use some such metal as brass or iron, except where very light screening is required, where aluminium is the most convenient. In this case the presence of copious primary β radiation renders the secondary β radiation of small importance. Experiments were also made with a brass screen about 3 mm. thick, covered on top with different thicknesses of material of low atomic weight. For small thicknesses visiting-cards (0·040 gram per sq. cm.) were found the most suitable, six of them being almost exactly equivalent to the same mass of leather. For greater thicknesses sheets of leather were employed. It was found that adding successive cards increased the ionisation until the total thickness of card or leather amounted to about 0·3 gram per cm. [equivalent to about 3 mm. of tissue]. Further increase caused a slight fall, due to absorption of γ rays. This apparently suggests that the practice of placing a material such as chamois between the metal screen and the skin is unwise; but, when allowance is made for the effect of distance, it will be shown later that this is not so. Practical experience confirms this latter view, as it is found that the presence of a sheet of chamois between the screen and the skin reduces the burning of the latter.

Stopping Power of various Substances.

The results of tests on various materials are shown by the curves in fig. 2, where the ordinates represent activity, and the abscissae mass per unit area of screen.

[1] E.g. Hackett, Scient. Trans. R.D.S., ix, Series II. 9, 1909.

Three curves are shown for card and leather, whose absorption per unit mass is almost identical. In curve *A* the activity of the bare tube is taken as 100, and each unit on the horizontal axis represents 1 gram per sq. cm.

FIG. 2.

[i.e. 1 cm. of animal tissue approximately]. The initial absorption of β rays is better shown on curve *B*, in which the horizontal scale is 10 times as open, i.e. for this particular curve each unit represents 0·1 gram per sq. cm. [1 mm

of tissue]. In curve *C* the vertical scale is 10 times as open, i.e. the activity of the bare tube is now 1000. The horizontal scale is normal. The use of these varying scales is rendered necessary by the great range of activities encountered with light screens.

Curves are also shown for aluminium, brass, and lead. In each case the scales are the same as for curve *C*, the activity of the bare tube being 1000, and the horizontal unit one gram per sq. cm. In using these curves the density of animal tissue may be taken as 1·0, that of aluminium as 2·7, brass 8·0, and lead 11·3. Thus 1 mm. of brass corresponds to 0·8 gram per sq. cm., and so on.

The following points may be noted:—

(1) The stopping power of a given mass of the screen for β rays increases with its atomic weight.

(2) The primary β rays are completely absorbed by 14 mm. of tissue, 5 mm. of aluminium, 1·5 mm. of brass, or 1 mm. of lead. These figures are obtained by dividing the abscissae for which the various curves become approximately horizontal by the densities of the corresponding screens.

(3) Owing to differences in secondary radiation, the total ionisation is not identical for various screens of just sufficient thickness to stop the primary β rays in each case. The peculiar crossing of the brass and lead curves is to be attributed to this cause, as the latter is raised by the large secondary radiation from the lead. It subsequently falls below the former again, owing to the greater absorption of γ rays by lead.

Greater thicknesses of leather could not be tested with the arrangement employed; but this is not a serious disadvantage, as in the calculations which follow the comparatively unimportant absorption of γ rays at such depths can be estimated with sufficient accuracy from the results obtained for brass, or taken from the figures obtained by other workers.

Tests were also made with an emanation tube enclosed in a standard serum needle 1·2 mm. external diameter, and various card and leather screens. These showed that the stopping power of the needle (apparently about 0·1 mm. thick) was very nearly equivalent to 1 mm. of tissue. This is used below.

Effect of Distance. Capillary in Needle.

The effect in the tissues at various distances from a needle containing an emanation tube has been calculated, and is shown in column A of the table on p. 475, in which a represents the distance from the centre of the needle. In making this calculation the emanation, instead of being distributed throughout a tube 15 mm. long by 0·6 mm. internal diameter, is

assumed to be concentrated at 15 axial points one millimetre apart. The stopping power of the wall of the serum needle is assumed to be equivalent to 1 mm. of flesh for normal rays, and proportionally more for oblique rays. For the latter the extra thickness of glass traversed must also be allowed for. Weighing showed that 0·1 mm. is a fair figure to assume for the thickness of wall of a typical emanation tube, as issued by the Royal Dublin Society Radium Institute. This is equivalent to 0·25 mm. of flesh. The outside radius of the serum needle being 0·6 mm., the total absorption between a point O on the axis and a point P at a radial distance a from O in the tissue is equivalent to that of $a + 1{\cdot}25 - 0{\cdot}6$, i.e. $a + 0{\cdot}65$ mm. of flesh. This is equivalent to the bare tube plus $a + 0{\cdot}4$ mm. of flesh. For another axial point O' distant b mm. from O we have distance

$$O'P = \sqrt{a^2 + b^2} \text{ and "equivalent" distance} = \frac{O'P}{a}(a + 0{\cdot}65) - 0{\cdot}25.$$

We look up the corresponding transmission factor from the "leather" curve, taking the unscreened activity as 1000, and multiply this by $\frac{m}{O'P^2}$, where m is the number of millicuries per mm. of the tube.

Summing the results for the 15 axial points, we obtain the activity for any given point P. The units are such that the activity due to one millicurie at one millimetre distance, with no other screening than the normal screening of the emanation tube wall, is 1000. The figures in the table are calculated for points opposite the centre of the capillary, so that the axial points considered, with the exception of the central one, occurred in pairs, thus simplifying the arithmetic.

Effect of Distance. Thick Surface Applicator.

A type of applicator which is considerably used in Dublin consists of a rectangular box made of brass, 3 mm. thick, the internal dimensions being 30 × 20 × 0·6 mm. To the inner surface of this a number of emanation tubes are fixed, with a little wax so as to give as uniform a distribution of activity as possible over the available area of 6 sq. cms. As the diameter of these tubes is about 0·8 mm., we may (making a small allowance for the wax) assume that the centre of the tube is 3·5 mm. from the nearer outer face of the box, and 3·5 mm. from the further outer face.

In estimating the activity at various depths due to such an applicator in contact with the skin the following approximations are made to simplify the calculation :—

(1) The box is assumed to be circular, of such a diameter so as to have the same area, and the calculations made for axial points only.

(2) The emanation is assumed to be confined to a plane parallel to the face of the box in contact with the skin.

(3) The activity of a parallel beam of rays which penetrate the box is assumed to be a linear function of the extra distance traversed. This will not introduce a large error for distances up to 10 cms. of tissue if a suitable absorption coefficient is chosen.

(4) Scattering is neglected [as in previous calculation].

Let r be the radius of the box, t its thickness, b the distance from the inner face of the box to the radioactive layer, and I the surface-density in millicuries per sq. mm.; then obviously the activity at an axial point a mm. below the surface is equal to

$$\int_0^r \frac{[K - (k_1 t + k_2 a)\sec\theta]\, 2\pi I x\, dx}{(b + t + a)^2 \sec^2\theta},$$

where

$$\tan\theta = \frac{x}{b + t + a},$$

and K, k_1, and k_2 are constants defining the absorption in brass and tissue.

Hence

$$\text{Activity} = 2\pi I \int_0^{\phi} [K - (k_1 t + k_2 a)\sec\theta]\tan\theta\, d\theta$$

$$= 2\pi I [K \log_e \sec\phi - (k_1 t + k_2 a)(\sec\phi - 1)],$$

where

$$\tan\phi = \frac{r}{b + t + a}.$$

This expression can be evaluated rapidly and with sufficient accuracy by means of a slide-rule, provided that ϕ—the angle subtended by the radius of the radioactive disc at the given point—is not too small. For small values of ϕ it is best to substitute

$$\frac{\tan^2\phi}{2} - \frac{\tan^4\phi}{4} \quad \text{for} \quad \log_e \sec\phi,$$

and

$$\frac{\tan^2\phi}{2} - \frac{\tan^2\phi}{8} \quad \text{for} \quad (\sec\phi - 1).$$

For very small values the expression reduces to

$$\pi I \tan^2\phi\, [K - (k_1 t + k_2 a)].$$

From inspection of the curves in fig. 2, and consideration of the known rate of absorption of the complex γ rays from *RaB* and *RaC*, we find $K = 10{\cdot}56$, $k_1 = 0{\cdot}32$, and $k_2 = 0{\cdot}04$ (assuming the mass coefficient of

absorption of brass and animal tissue for γ rays to be approximately the same). In all cases considered $t = 3{\cdot}0$ mm.

The figures so obtained would represent the activity if the secondary radiation in the flesh were identical with that on the skin in contact with a brass radiator, as K was determined from the "brass" curve. In the interior the increased secondary radiation due to the tissue raises the total activity by about 10 per cent., so in the results shown below this correction has been applied to all depths exceeding 3 mm. Appropriate corrections are applied for smaller depths, no correction being required at the surface.

Three sets of figures have been worked out and are shown in columns B, C, and D of the following table, the corresponding conditions being explained below:—

a	A	B	C	D	a	A	B	C	D
mm.					mm.				
0	—	1·24	0·62	0·093	15	0·46	0·225	0·15	0·053
0·5	—	1·18	0·60	0·093	16	0·41	0·205	0·14	0·051
0·6	620	—	—	—	17	0·37	0·19	0·13	0·049
1	227	1·12	0·58	0·093	18	0·33	0·175	0·12	0·047
2	58	0·99	0·525	0·091	19	0·30	0·16	0·115	0·045
3	23	0·87	0·475	0·088	20	0·27	0·15	0·105	0·044
4	11·6	0·76	0·425	0·084	25	0·17	0·105	0·076	0·037
5	6·7	0·66	0·375	0·080	30	0·117	0·075	0·058	0·031
6	4·2	0·58	0·34	0·077	35	0·084	0·057	0·044	0·026
7	2·8	0·52	0·305	0·074	40	0·064	0·044	0·036	0·022
8	1·93	0·46	0·275	0·071	45	0·050	0·035	0·030	0·019
9	1·41	0·405	0·25	0·068	50	0·039	0·027	0·023	0·016
10	1·08	0·36	0·23	0·065	60	0·026	0·019	0·016	0·012
11	0·87	0·325	0·21	0·062	70	0·018	0·014	0·012	0·009
12	0·72	0·295	0·195	0·060	80	0·013	0·010	0·009	0·007
13	0·61	0·27	0·18	0·057	90	0·010	0·008	0·007	0·006
14	0·53	0·245	0·165	0·055	100	0·008	0·006	0·005	0·004

Explanation of Table.

a is the distance in millimetres of the point in the tissue at which the activity is given in the other columns. For the figures in column A (emanation needle) a is the distance from the axis of the needle; for the other columns, a is the distance from the surface of the skin.

The activity due to a point-charge of one millicurie at a distance of one millimetre, with no screening except the glass of the emanation tube, is taken as 1,000.

A. Activity due to 10 mc. in a tube 15 mm. long inside a standard serum needle.

B. Activity due to 10 mc. uniformly distributed over 6 sq. cm., the emanation tubes being attached to the bottom of the brass box, 3 mm. thick, which is placed in contact with the skin.

C. Activity due to 10 mc. uniformly distributed over 6 sq. cm., but with the emanation tubes attached to lid of the box, leaving an air space of 5 mm. between the tubes and the inner surface of the bottom of the box.

D. Activity due to 10 mc. uniformly distributed over 100 sq. cm., the tubes being placed as in C.

General Conclusions.

It is evident that the conditions specified under D could not be conveniently realized with a single application; but a similar (though not an identical) effect can be obtained by successive applications of the brass box, covering all parts of the required area in succession for equivalent times. The total dose of millicurie hours must then be used in arriving at the resultant action. For example, if we take the figures in the table as measuring the effect produced by a ten-millicurie-hour dose, the effect of a total dose of 200-millicurie-hours uniformly distributed over 100 sq. cms. would be 20 times the corresponding figure in column D.

The following points may be noted from the above figures:—

(1) The very great activity of emanation in needles at moderate distances.

(2) The great reduction in surface effect caused by increasing the distance of the capillaries from the skin.

(3) The still greater reduction in surface effect due to increase of area.

The effect of interposing material such as chamois between the applicator and the skin is nearly, but not quite, obtained by measuring "a" from the outer surface of the chamois, i.e. by treating the chamois as the outer layers of tissue in the above table. Thus, with conditions B above and 1 mm. of chamois interposed, the activity on the surface of the skin would be 1·12 instead of 1·24. This shows the effect of chamois in acting as a distance piece.

This is not quite accurate, as chamois, being much less dense than living animal tissue, the increase in secondary radiation is much slower in it, so

that the activity at the base of a sheet 1 mm. thick would be less than 1·12. It would appear that the more porous the material used between the metal and the skin the less should be the burning effect upon the latter.

In the case of treatment with several parallel needles, each containing a tube 15 mm. long, the distribution of activity in a perpendicular plane through their centres can be found by summing the effects of the separate needles for any required point. Where the area of irradiation is increased by the use of long needles, which are partially withdrawn at intervals, so as to move the emanation tube to a new position on the axis, the effect is similar to that of a long emanation tube, and could be calculated by the same method as that used above for the short tube.

XXXVI.

THE INFLUENCE OF FEEDING ON MILK FAT.

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Each individual species of mammal produces milk of composition peculiar to its own group, but among domesticated animals the proportion of some of the constituents, especially that of fat, to the total milk yield varies considerably in the different varieties of each species, in the different strains inside a variety, and, further, even in the individuals of any single strain. The variation in the percentage of fat in the milk of cows and goats, for instance, is practically due to the selection exercised by man; indeed it has long been recognised that selection is the principal method available to the stock-breeder for raising milk fat percentage.

The influence of feeding on milk fat has been the subject of frequent investigation, but very little precise information on the subject is available. Speir [1894, 6 and 7] compared a large number of rations, all liberal in quantity, with one another for the purpose of milk and butter fat production in the dairy cow, and came to the general conclusion that the criterion of efficiency in a ration is its total dry matter. But he was of opinion that some foods tend to increase the milk yield, while others tend to increase the milk fat principally. Fresh grass and brewers' grains, he states, tend to increase the milk yield at the expense of the percentage of butter fat; on the other hand, vetches and decorticated cotton cake tend to increase the percentage of fat at the expense of milk yield. It is significant that both of these foods contain a high proportion of protein; in fact, Speir concludes that rations with a very high albuminoid ratio seem to have a depressing effect on the milk yield. On the other hand, Crowther [1906], reviewing the work done in Great Britain for some years previously, makes the following statement: "Such changes as may possibly be effected in the quantitative composition of milk by change of food are only very slight, provided, of course, the rations prior and subsequent to the change are suitable in nature and in quantity." Wing and Foord [1904] record an attempt to increase the fat in milk by means of liberal feeding, and state that in a herd of poorly

fed cows the subsequent feeding of an abundant ration resulted in an increase in the percentage of fat as well as an increase in the total milk and total fat. The experiment continued over a number of years. Yet Rühle [1919] and Pritzker [1919] find, from a large number of analyses made during the period 1914–18, no evidence to show that food deficiency causes a decrease in the fat content of milk. Data collected by the Dairy Section of the Department of Agriculture and Technical Instruction for Ireland does not lend support to this view, but is rather in agreement with the work of Wing and Foord. Referring to the effect of water in the food on the composition of milk, Turner, Shaw, Norton, and Wright [1916] state that the water content of a ration has no effect on the composition of milk yielded therefrom; and Berry [1921] comes to the same conclusion. It is evident that there is no unanimity of opinion among previous investigators as to the effect of feeding on milk fat.

Much of the work referred to was done on good condition cattle, continuously getting abundant supplies of food, so that the effect of the changes in diet was difficult to detect. Besides, changes were made by completely substituting one food for another, so that usually more than one food constituent was involved. For instance, the substitution of brewers' grains for cotton cake involves a change in the quantity of carbohydrates and fats, and in the quantity and quality of the proteins. Thus more than one variable was introduced, and there was not a clear comparison of the effect of one food ingredient with that of another. Realizing the necessity for conducting such an investigation under conditions approximating to laboratory control, it was decided in this investigation to substitute goats for cows. To the diet of these animals the individual food constituents could be added at comparatively small cost, while at the same time sufficient milk is yielded to afford a considerable margin for fluctuation resulting from experimental changes in conditions. In the goat, as in the cow, the milk yield is highest at the beginning of lactation, and it declines gradually towards the end. The lactation period, in the case of the old Irish breed, usually begins in April and terminates about December. As in the cow also the percentage of fat in the milk tends to increase as lactation advances, and the weight of the animal's body similarly increases towards the termination of the milk flow, especially with liberal feeding. The general procedure in this investigation was first to observe the quantity of food which just maintained the animal's weight and at the same time yielded a constant flow of milk, and then test the effect of adding to this "milk and body maintenance" ration different quantities of individual food constituents. Then, when the effect of an addition to the ration was determined, the effect of the withdrawal of that addition was subsequently investigated. Extra food assimilated above the "milk and

body maintenance" level goes to increase either the milk, or some of the constituents thereof, or the weight of the animal, or all three. Consequently right through the period of investigation records were kept of milk, milk fat, and the animal's weight. The milk was weighed and the fat percentage determined daily, and the animals were regularly weighed once a week.

Figs. 1, 2, and 3 record the diet and changes therein of three experimental goats during the period of investigation, and give a graphical representation of the results from the experiment.

The results obtained from this investigation are interpreted as follows :—

Goat 1.

1. Reduction in daily ration (change from ration A to B) produces—
   (*a*) No change in milk yield ; as a matter of fact, the already increasing yield continues to increase for a short time.
   (*b*) Reduction in daily per cent. fat of 1·25 (4·75 to 3·5).
   (*c*) Reduction in daily total fat of 0·015 lb. (0·130 to 0·115).

2. Addition of 0·47 lbs. soya fat to daily ration (change from ration B to C) produces—
   (*a*) No change in milk yield.
   (*b*) Increase in daily per cent. fat of 0·75 (3·5 to 4·25).
   (*c*) Increase in daily total fat of 0·035 lb. (0·115 to 0·150).

2_1. Withdrawal of roots from ration (change from ration C to D) produces—
   (*a*) Considerable reduction in milk yield.
   (*b*) „ „ daily per cent. fat.
   (*c*) „ „ daily total fat.

3. Addition of 0·5 lbs. soya fat to daily ration (change from ration E to F) produces—
   (*a*) No change in milk yield.
   (*b*) Increase in daily per cent. fat of 1·75 (3·75 to 5·5).
   (*c*) Increase in daily total fat of 0·05 lb. (0·09 to 0·14).

4. Further addition of 0·5 lb. soya fat to daily ration (change from ration F to G) produces—
   (*a*) No change in milk yield.
   (*b*) Increase in daily per cent. fat of 1·0 (5·5 to 6·5).
   (*c*) Increase in daily total fat of 0·025 lb. (0·140 to 0·165).

5. Reduction in daily ration (change from ration G to H) produces—
   (*a*) No change in milk yield.
   (*b*) Reduction in daily per cent. fat of 2·0 (6·5 to 4·5).
   (*c*) Reduction in daily total fat of 0·075 lb. (0·165 to 0·090).

Fig. 1—Goat 1.

Daily Ration.

A—(37 days). Hay ad lib. Mangels, 1 stone. Crushed oats, bran, and dried grains, 1½ lbs.

B—(21 days). Hay, 1 lb. Mangels 10 lbs. Skim-milk powder, 1·28 lbs. [Reduction on previous ration.]

X—(14 days). (Transition to new ration.)

C—(24 days). Hay, 1 lb. Mangels, 10 lbs. Skim-milk powder, 1·28 lbs. Fat (soya), 0·47 lb. [0·47 lb. soya fat added to previous ration.]

D—(11 days). Hay, 1 lb. Skim-milk powder, 1·28 lbs. Fat (soya), 0·47 lb. [Withdrawal of roots from ration.]

Y—Irregular, owing to failure of supplies.

E—(21 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb.

F—(20 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. Fat (soya), 0·5 lb. [0·5 lb. soya fat added to previous ration.]

G—(23 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. Fat (soya), 1·0 lb. [0·5 lb. soya fat added to previous ration.]

H—(17 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. [Reduction on previous ration.]

GOAT 2.

1. Reduction in daily ration (change from ration A to B) produces—

(*a*) No change in milk yield.
(*b*) Reduction in daily per cent. fat of 0·25 (3·75 to 3·5).
(*c*) Reduction in daily total fat of 0·015 lbs. (0·135 to 0·120).

2. Addition of 1·06 lbs. wheaten starch to daily ration (change from ration B to C) produces—

(*a*) No change in milk yield.
(*b*) Increase in daily per cent. fat of 0·75 lbs. (3·5 to 4·25).
(*c*) Increase in daily total fat of 0·03 lbs. (0·12 to 0·15).

3. Addition of 1·13 lbs. wheaten starch to daily ration (change from ration E to F) produces—

(*a*) No change in milk yield.
(*b*) Increase in daily per cent. fat of 0·75 (5·0 to 5·75).
(*c*) Increase in daily total fat of 0·02 lbs. (0·125 to 0·145).

3_1. Substitution of 0·5 lbs. fat for 1·13 lbs. starch (change from ration F to F_1) produces—

(*a*) No change in milk yield.
(*b*) Increase in per cent. fat.
(*c*) „ total fat.

} The fact that this increase is of short duration, and that the yields tend to return to original level, discounts this result.

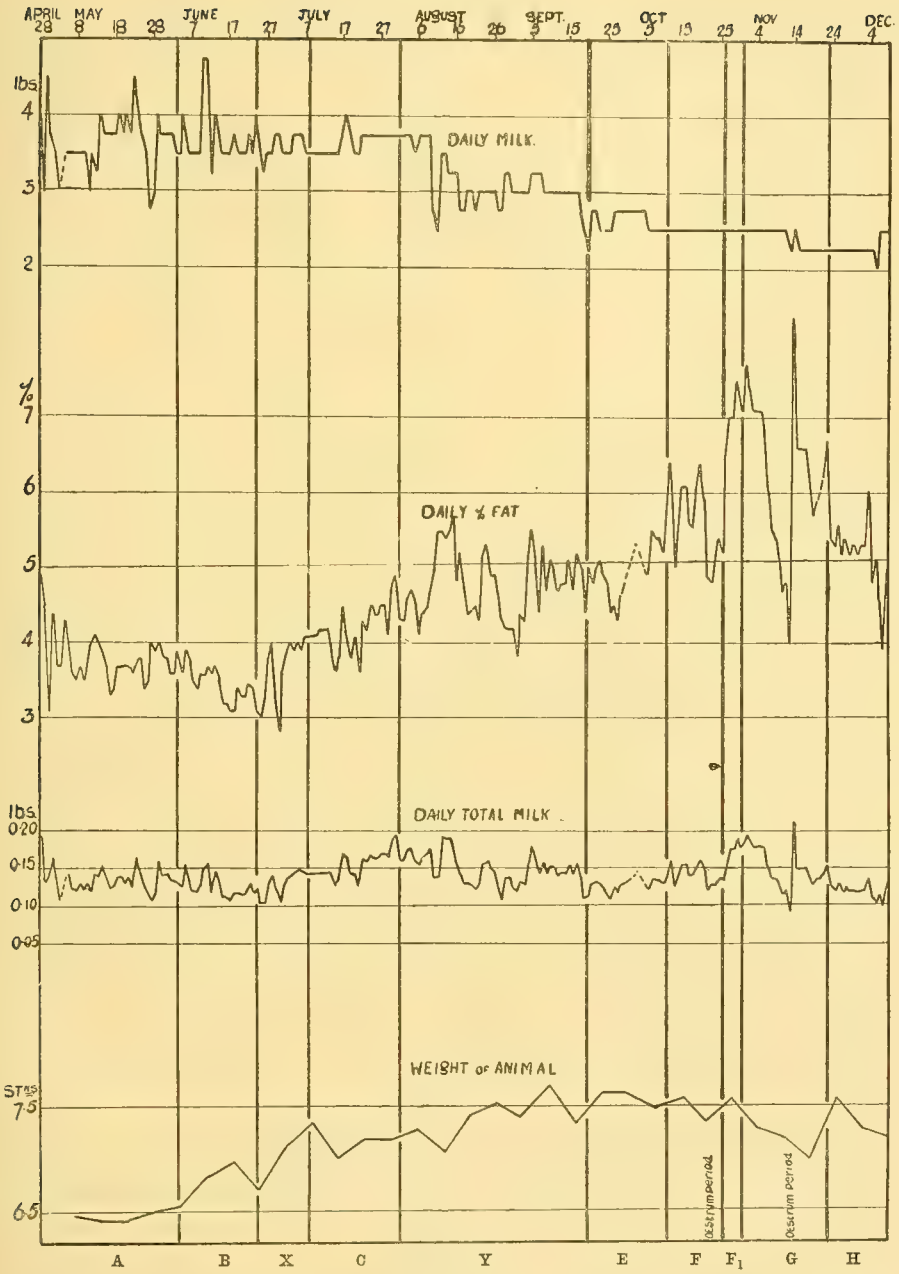
4. Substitution of 1·13 lbs. casein for 0·5 lbs. fat, and hence for 1·13 lbs. starch (change from ration F_1 to G), produces—

(*a*) No change in milk yield as compared with ration F.
(*b*) „ „ daily per cent. fat „ „ „ „
(*c*) „ „ daily total fat „ „ „ „

5. Reduction in daily ration (change from ration G to H) produces—

(*a*) No change in milk yield.
(*b*) Reduction in daily per cent. fat of 0·5.
(*c*) Reduction in daily total fat of 0·025 lbs. (0·145 to 0·120).

Fig. 2—Goat 2.



Daily Ration.

A—(37 days). Hay ad lib. Mangels, 1 stone. Crushed oats, bran, and dried grains, 1½ lbs.

B—(21 days). Hay, 1 lb. Mangels, 10 lbs. Skim-milk powder, 1·28 lbs. [Reduction on previous ration.]

X—(14 days). (Transition to new ration.)

C—(24 days). Hay, 1 lb. Mangels, 10 lbs. Skim-milk powder, 1·28 lbs. Starch (wheaten), 1·06 lbs. [1·06 lbs. starch added to previous ration.]

Y—Irregular, owing to failure of supplies.

E—(21 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb.

F—(20 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. Starch, 1·13 lbs. [1·13 lbs. starch added to previous ration.]

F1—0·5 lb. fat replaces the starch of previous ration.

G—(23 days). Hay, 1 lb Turnips, 10 lbs. Oats, 0·83 lb. Casein, 1·13 lbs. [1·13 lbs. casein replaces the 0·5 lb. fat of previous feed, and the 1·13 lbs. starch of the ration previous to that.]

H—(17 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. [Reduction on previous diet.]

Goat 3.

1. Reduction in daily ration (change from ration A to B) produces—

(*a*) No change in milk yield.
(*b*) Reduction in daily per cent. fat of 0·75 (4·0 to 3·25).
(*c*) Reduction in daily total fat of 0·02 lb. (0·175 to 0·150).

2. Addition of 0·5 lb. butter fat to ration (change from ration B to C) produces—

(*a*) No change in milk yield.
(*b*) Increase in daily per cent. fat of 1·0 (3·25 to 4·25).
(*c*) Increase in daily total fat of 0·04 lb. (0·15 to 0·19).

3. Addition of 1·13 lbs. casein to daily ration (change from ration E to F) produces—

(*a*) No change in total milk yield.
(*b*) Increase in daily per cent. fat of 0·75 (4·5 to 5·25).
(*c*) Increase in daily total fat of 0·025 lb. (0·110 to 0·135).

4. Further addition of 0·5 lb. fat to daily ration (change from ration F to G) produces—

(*a*) No change in milk.
(*b*) Increase in daily per cent. fat of 1·0 (5·25 to 6·25).
(*c*) Increase in daily total fat of 0·025 lb. (0·135 to 0·160).

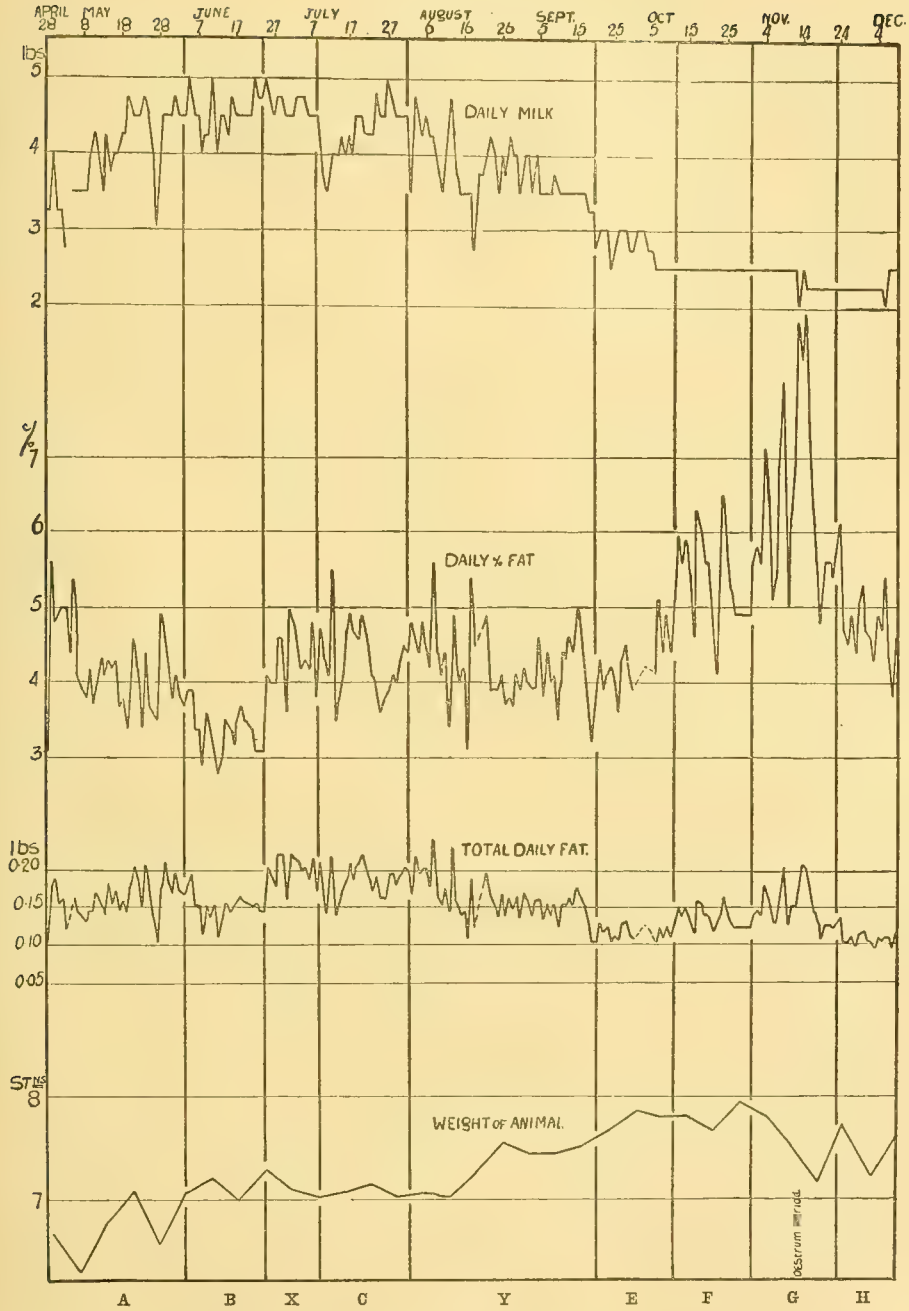
5. Reduction in daily ration (change from ration G to H) produces—

(*a*) No change in milk yield.
(*b*) Reduction in daily per cent. fat of 1·5 (6·25 to 4·75).
(*c*) Reduction in daily total fat.

The foregoing results lead to the following conclusions:—

1. By considerably reducing the ration the total daily yield of fat is reduced. If, at the same time, there is little or no reduction in milk yield, the percentage of fat in the milk is lowered. This occurs in the early stages of lactation, when the mammary gland is very active, and towards the end of the lactation, when the milk flow is already reduced to a minimum. Obviously, a fall in milk yield, accompanied by a fall in total fat, may leave the percentage of fat unchanged; and conceivably a considerable fall in milk occurring at the same time as a reduction in total fat may produce an increase in the percentage of fat in the milk.

Fig 3—Goat 3.



Daily Ration.

A—(37 days). Hay ad lib. Mangels, 1 stone. Crushed oats, bran, and dried grains, 1½ lbs.

B—(21 days). Hay, 1 lb. Mangels, 10 lbs. Skim-milk powder, 1·28 lbs. [Reduction on previous ration.]

X—(14 days). (Transition to new ration.)

C—(24 days). Hay, 1 lb. Mangels, 10 lbs. Whole milk powder, 1·75 lbs. [·45 lb. butter fat added to previous ration.]

Y—Irregular, owing to failure of supplies.

E—(21 days). Hay, 1 lb Turnips, 10 lbs. Oats, 0·83 lb.

F—(20 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. Casein, 1·13 lbs. [1·13 lbs. casein added to previous ration.]

G—(23 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. Casein, 1·13 lbs. Fat, 0·5 lb. [0·5 lb. fat added to previous ration.]

H—(17 days). Hay, 1 lb. Turnips, 10 lbs. Oats, 0·83 lb. [Reduction on previous ration.]

2. By adding butter fat, soya fat, wheaten starch, or casein to a "milk and body maintenance" ration the total fat in the daily milk is increased. In all the tests recorded in this investigation the milk flow remains unaffected by the addition of these single food substances; but the percentage of fat in the milk is increased. That is to say, the percentage of fat in the milk is raised, not only by the addition of fat to the food, but also by the addition of carbohydrate or protein. Obviously, if an increase in the milk flow occurs proportionate to the increase in the total fat, the percentage of fat in the milk is unchanged.

3. In the production of butter fat in milk, starch, casein, and fat (both butter and soya) replace one another; but the quantities which replace each other cannot yet be definitely stated. In the early part of lactation 0·45 lb. of soya fat produced an increase of 0·035 lb. of fat in the milk of goat 1; 1·06 lb. starch (that is about two and a quarter times more starch than fat) produced an increase of 0·03 lb. milk fat in goat 2; and 0·45 lb. butter fat produced an increase of 0·04 lb. milk fat in goat 3. In the second half of lactation 0·5 lb. soya fat produced an increase in the total milk fat of 0·05 lb. in goat 1, 1·13 lb. starch (about two and a quarter times the weight of fat), an increase of 0·02 lb. milk fat in goat 2, and 1·13 lb. casein an increase of 0·025 lb. milk fat in goat 3. In one case soya fat was just slightly better and in another it was twice as good as two and a quarter times its weight of starch. Butter fat was slightly better than soya fat for milk fat production, but the test was too limited to draw a general conclusion. It was thought that butter fat would be much superior for this purpose to soya fat, because of its content of vitamin A; but perhaps sufficient vitamin A was already supplied in the remainder of the ration to prevent a possible difference between the effects of the two fats becoming apparent.

In goat 2 the substitution of fat for starch in ration F_1 had a peculiar result. Possibly this is temporary, and the duration of this test was too short to allow of a general conclusion. When, however, casein replaces the fat (ration G, goat 2), the total fat in the milk is similar to that produced by an equal weight of starch. Thus right through the experiment casein and starch replace one another in equal proportions. Evidently this can only hold where sufficient protein is already supplied in the "milk and body maintenance" ration to contribute to the production of the protein moiety of the milk yielded, and otherwise maintain nitrogenous equilibrium. Further work remains to be done on the quantitative replacement of fats and carbohydrates in food for the purpose of milk fat production.

4. While an addition to the "milk and body maintenance" ration

increases the butter fat, a further similar addition does not increase the butter fat to the same extent. In goat 1, the addition of half a pound of fat to the ration (ration E to F) increased the milk fat by 0·05 lb.; a further addition of half a pound caused an increase of only 0·025 lb. milk fat. Even where the diet already contains a large proportion of protein (ration F, goat 3) the further addition of half a pound of fat to the diet gave an increase of only 0·025 lb. milk fat. The percentage of fat in milk can obviously be raised by extra feeding to a maximum; and, if fat percentage is the only consideration, it might be said that the maximum is reached according to the law of diminishing returns. But, as the ration is increased, body weight and total milk may be also increased, and a successively larger proportion of the food utilized for these purposes. Since, according to Nils Hansson [1916] and Wilson [1920], the law of diminishing returns does not hold in the production of beef and milk, neither is it likely to hold in the production of butter fat.

Summary.

In the case of a lactating goat—

1. A considerable reduction in the ration may cause a decrease in the percentage of fat in the milk. This occurs when the total fat yield is decreased at the same time as the milk yield remains unchanged, or when the proportionate decrease in the total fat is greater than the decrease in milk.

2. The addition of a concentrate to a ration may cause an increase in the percentage of fat in milk. This occurs when the total fat yield is increased, while the milk yield remains unchanged, or when the proportionate increase of total fat is greater than the increase in milk.

3. In effecting an increase in the total and in the percentage of butter fat in milk, starch, fat (soya and butter), and protein can replace one another. After the necessary minimum of protein is supplied, starch and casein replace one another for that purpose in equal parts.

4. There is a maximum milk fat percentage, and, as this limit is approached, the extra food added to the ration produces a successively decreasing addition to the milk fat percentage, but at the same time a successively increasing addition to the body weight or milk yield, or both.

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XXXVII.

ON A NEW METHOD OF GAUGING THE DISCHARGE OF RIVERS.

By J. JOLY, Sc.D., F.R.S., F.T.C.D.

[Read February 28. Published April 13, 1922.]

The new method is based on the principle underlying "chemical hydrometry." This principle may be simply expressed as follows:—

Suppose it were required to estimate the quantity of water contained in a large tank the volume of which it was difficult to determine by mere geometric measurements. By means of chemical hydrometry the quantity of water is easily found. A known weight of any suitable soluble salt is stirred into the tank, so that there is uniform distribution of the salt throughout the water. We then abstract a known volume V of the water, and by titration or other means estimate how much of the salt is contained in this volume of water. Now, if this amounts to $\frac{1}{n}$th of the salt put into the tank, the volume of water in the tank must be $n \times V$.

This method has been applied to the discharge of rivers. A tank is erected at some convenient point on the river. In this tank a large volume of water is stored, and into it is stirred a heavy charge of the salt; generally chloride of sodium. A pipe is led from the tank into the river, and the salt solution is fed slowly, and at a uniform rate, from the tank, escaping from perforations in the pipe and intermingling with the current. At a point some distance down stream samples of water are taken at intervals. These samples are titrated; and, knowing the rate at which the salt has been fed into the river, the rate of discharge can be calculated.

Very accurate results are obtained by this method. The error can be reduced below 1 per cent. It is said to be superior in accuracy to weir-measurements, and very much superior in accuracy to measurements based on current meters. A very full account of the method is given by B. F. Groat, M.AM.SOC.C.E., in the Proceedings of the American Society of Civil Engineers, vol. xli, November, 1915.

A study of Mr. Groat's paper reveals the advantages and disadvantages of the method. Chief of the latter is the cumbersome nature of the preparations which have to be made, due to the large amount of salt required.

Moreover, the cost is considerable, owing to the scale on which the salt must be supplied.

It was in connexion with the important problems arising in relation to Irish water-power utilization, as recently put forward by Sir John Purser Griffith before this Society, that I thought of the following procedure. At the time I was in ignorance of the fact that the principle involved had ever before been used or thought of.

I propose to utilize, in determining river discharge, the extraordinary accuracy with which radioactive measurements can be effected. A very simple form of electroscope suffices to determine a quantity of radium to the billionth part of a gram. The apparatus costs a very few shillings. If, now, in place of introducing salt by the hundredweight into the river, we flow into the river a few litres of a solution containing a trace of radium, and taking samples down stream examine them by the electroscope, the discharge of the river may be determined.

In order to reduce the working conditions to figures, I take the case of the Poulaphuca and Golden Falls on the Upper Liffey. The flow I take as 20,000 cubic feet per minute.

The constant of the electroscope I take as $0{\cdot}54 \times 10^{-12}$. That is to say, this quantity of radium, or rather the emanation in equilibrium with it, will cause the gold leaf of the electroscope to show a gain in rate of fall of 1 scale division per hour. I have made many such electroscopes. We require to know how much radium is to be put into the river, so that we can estimate the discharge to 1 per cent.; and I assume that the feed of radioactive water into the river is maintained for twenty minutes.

Suppose we withdraw samples of 10 litres volume for testing by the electroscope. To evaluate the radium to 1 per cent., it must increase the rate of fall of the leaf of the electroscope by 100 scale divisions per hour. That is, the 10 litres must contain 54×10^{-12} gram radium; i.e., there must be $5{\cdot}4 \times 10^{-12}$ gram radium per litre of water passing down the river. Now, the flow of the river as assumed is about 600,000 litres per minute. The quantity of radium fed in per minute must therefore be $6 \times 10^5 \times 5{\cdot}4 \times 10^{-12} = 32 \times 10^{-7}$ gram. *q*, *p*; and for twenty minutes' flow we require 64×10^{-6} gram radium: that is, 0·064 milligram must be put in.

Now, the most economical form in which the radium can be supplied is pitchblende, the mineral oxide of uranium. In this ore 200 milligrams of radium are associated with 1,000 kilos of the mineral, from which we find that 0·01 milligram of radium are contained in 50 grams of the ore. 300 grams are required to supply 0·06 milligram.

This quantity of radium—pure—would cost about 36s.; in the ore it should be one-sixth or one-eighth part of this, i.e., five or six shillings.

If a two per cent. determination was deemed sufficiently accurate, and a fifteen-minute feed into the river, a hundred grams of the crude ore would suffice, and the cost would be correspondingly reduced.

As regards details, I propose to bring the pitchblende into solution by powdering it and adding nitric acid. It dissolves readily. The charge is then diluted with water up to about two gallons, i.e., the full of a petrol tin. In this form it is brought to the scene of operations. The stopper is then replaced by one which carries a copper tube dipping to the bottom of the tin. This tube is coupled to a similar small-bore tube to be laid out across the current. It is pierced with fine holes at intervals, say of 6 inches. Air pumped into the tin by an ordinary tyre-pump serves to expel the liquid. The current is steadied by having in circuit an indiarubber bag, which is kept inflated to a constant pressure, as read by a small air-pressure gauge. The air-pressure being considerable, the small effect of variation in hydrostatic head will be negligible.

I think a very little time spent on experiments in the laboratory will suffice to bring these practical details into working order.

When the samples are collected (each sample will about fill a petrol tin) and brought back to the laboratory, they are stored in ordinary boiling flasks for ten or twelve days. The emanation is then boiled off, being caught in a small exhausted bulb, from which it is introduced into the electroscope. At the end of three hours the electroscope is read, and the river discharge is then immediately deducible. If thought desirable, the samples may be evaporated down to any required extent. No error is introduced by this process. It is necessary to carry out these operations in a laboratory free from radium contamination.

XXXVIII.

ON A VARIETY OF PINITE OCCURRING AT BALLYCORUS, CO. DUBLIN.

By LOUIS B. SMYTH, M.A., Sc.B.,
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[Read February 28. Published April 13, 1922.]

Introduction.

Some months ago Mr. J. C. Davison, of the Engineering School, Trinity College, Dublin, brought me for identification a green mineral, found at the old lead mines of Ballycorus. It appears not to have been described before.

Mode of Occurrence.

A visit to the locality showed that the substance occurs in the granite blocks thrown out during mining operations, and lying about in and around the large cutting, near the chimney, at the top of the hill. The excavation is at the junction of granite and schist. All stages can be found between typical granite and a thoroughly green rock.

Results of Tests.

The following are the results of tests made on the most translucent, lustrous fragments :—

Compact. Unctuous.

H = 2·5. G = 2·780.

Lustre.—Fatty.

Colour.—Oil green to pale yellowish green. Translucent.

Insoluble, and does not gelatinize in hydrochloric or nitric acids, or n caustic potash.

Decomposed by hot concentrated sulphuric acid, with separation of powdery silica. Alum is deposited when the filtered acid is evaporated.

In the closed tube gives off water easily, and becomes white. Some fragments darken. Occasionally decrepitates slightly.

BB.—Infusible, turns white, and does not colour the flame. With cobalt nitrate gives a strong blue.

Details of Tests.

Hardness tests required special care owing to the presence of minute grains and veins of quartz. The salient angles of chips were used to scratch good cleavage surfaces of selenite, Iceland spar, &c. In one sample, for

instance, there were four convenient angles. Three of these scratched Iceland spar ; the fourth would not. The latter corner scratched selenite.

Measurements of specific gravity were made by means of methylene iodide, diluted with xylol, on very small particles obtained by crushing. The specific gravity of the liquid was found with a Westphal balance. The highest results are considered the most reliable, for (1) the microscope showed that the chief impurity was quartz, and the specific gravity always came out higher than that of quartz ; (2) dull specimens known to be impure gave low results ; (3) the more finely divided material gave a higher proportion of heavy grains.

Chemical Analysis.

The result of a chemical analysis of five or six grams of the most carefully picked material is shown in column I of the table. One chip of the same lot was sliced for the microscope in order to gain an idea of its purity. It contains a remnant of a disintegrating felspar crystal and some minute granules of quartz, but the great bulk of it is of one kind of material of uniform texture.

	I.	II.	III.
SiO_2	49·54	46	47
Al_2O_3	34·86	33	32
Iron Oxide	0·24	4	3
CaO	tr.	0	1
MgO	0·72	1	2
Na_2O	0·78	1	1
K_2O	9·00	9·5	8
Li_2O	tr.	—	—
P_2O_5	?	—	—
CO_2	0·00	—	—
F	0·00	0·5	—
Moisture	0·90	5	6
Loss on ignition	3·90 (4·80)		
	99·94	100	100

I.—Pinite, Ballycorus, Co. Dublin.

II.—Average of 19 analyses of muscovite quoted by Dana (Syst. Min., 6th ed., pp. 617–8, analyses 1 to 19, inclusive. 1911).

III.—Average of 12 analyses of pinite (*loc cit.*, p. 622).

Microscopical Characters.

In thin section the mineral still appears compact when viewed with a pocket lens. With a magnification of seventy diameters it exhibits a granular structure, and appears to have higher refraction than quartz. Between crossed nicols it is seen to be birefringent, the field being finely speckled. A higher power shows that in places the structure consists of rough radial aggregates, in which the components may occasionally be seen to have straight extinction.

Identification.

Comparing the analysis with column II of the table, it will be seen that there is good agreement with an average muscovite. The latter, however, is not affected by acids, whereas the Ballycorus mineral is completely decomposed by hot concentrated sulphuric acid.

The term Pinite is applied to a number of compact substances, which are generally alteration products, and have a composition similar to that of muscovite. Most, if not all, of them differ from muscovite, and agree with our mineral, in being decomposable by sulphuric acid. As was to be expected, since they are generally impure substances, none of the named varieties was found to agree in all points with the Ballycorus mineral, though many come near it.

The best agreement seems to be with pinitoid. That mineral, according to A. Knop,[1] is a basic silicate, mica-like in composition, containing water, decomposable by hot sulphuric acid, micro to cryptocrystalline, of usually earthy to dense compact habit, of a leek-, oil-, or greyish-green to whitish colour, which may pass over into various shades of red. Specific gravity, 2·788 ; H, 2·5. It is a secondary mineral formed by hydration, which frequently occurs as pseudomorphs after felspar in altered porphyry.

So far this might apply to the Ballycorus mineral, except that it was not observed in shades of red. Knop's analysis would account for this, and reveals a considerable difference in composition, for the pinitoid analysed gave 8·84 per cent. oxide of iron against 0·24 per cent. in our mineral. Pinitoid, too, is low in potash, 5·85, as compared with 9·00.

Column III of the table is the mean of the twelve pinite analyses given by Dana.[2] Comparison with column I shows the close agreement. As a matter of fact, all the figures for the Ballycorus mineral are inside the extremes occurring in those analyses.

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[1] "Neues Jahrbuch für Mineralogie," etc., p. 558. 1859.
[2] *Loc. cit.*, p. 622.

The mineral under discussion, then, is evidently a pinite. It seems to me unnecessary to invent any more definite term.

Since killinite, another variety of pinite, occurs, also near the granite margin, at Killiney, a few miles from Ballycorus, we must distinguish it from the present mineral. It differs most distinctly (1) in being pseudomorphous after spodumene, (2) in being fusible before the blowpipe.[1]

Origin and Relations.

A number of thin slices of granite in various stages of alteration were prepared. One fresh-looking specimen contains abundant allotriomorphic microcline, with strong, typical cross-hatching, only slightly cloudy on certain laminae, and often including idiomorphic crystals of the other felspars. There is much albite, mostly speckled over with alteration products. What appears to be orthoclase is much altered, the secondary material usually occupying all the centre of the crystal, and agreeing in appearance with the pinite. The quartz is in groups of grains, and there is a fair amount of muscovite. Cataclastic structures are evident. The quartz is in places finely granular, and the mica bent and broken. In a shear zone the latter seems to be ground to a fine granular paste, which is doubtfully distinguishable in places from the pinite. A little galena is present.

Slices containing a considerable amount of pinite appear to show that it originates, at least chiefly, from felspar. The latter often occurs like an archipelago surrounded by a sea of the alteration product, the islands being optically parallel. In this material the felspars have rather indefinite optical characters. Considerable fragments may appear untwinned, but a higher magnification often reveals the microcline structure on a minute scale in spots, mostly at the edges. What appears to be secondary lamellar twinning is often seen. In several cases there cross such felspars broad bands, suggesting shearing planes, distinguished by more intense alteration. Quartz is generally abundant, often showing strain shadows, which are sometimes arranged fanwise.

A slice made from a piece of rock having a fairly uniform green colour, but a dull lustre, was found to consist of pinite with abundant, but small, ragged quartz grains, a very few similar fragments of felspar, and still fewer of muscovite.

A remarkable relation between quartz and pinite is observed in some

[1] Thos. Taylor, "Account of a New Mineral Substance discovered at Killiney, in the vicinity of Dublin," Trans. Roy. Ir. Acad., vol. xiii, p. 61. 1818.
T. Thompson, "Outlines of Mineralogy," vol. i, p. 330. 1836.

slices, the latter being in rosette-like patches within the quartz grains in the plane of section, or biting into their edges, as if growing at the expense of the quartz. This is extremely unlikely, especially as no trace of fluorine was found in the analysed material, though looked for specially.

It is probable that the silica, thrown out of the felspar as it alters into pinite, crystallises round the latter, and is moulded upon it.

That quartz is so produced is well known. Rosenbusch,[1] referring to orthoclase "altered to muscovite (pinitoid)," states that "quartz is almost always mixed with these pseudomorphs in variable amounts."

[1] "Microscopical Physiography of Rock-making Minerals," Rosenbusch-Iddings, 3rd ed., p. 314. 1893.

XXXIX.

ON THE LIFE-HISTORY AND BIONOMICS OF THE FLAX FLEA-BEETLE (*LONGITARSUS PARVULUS*, PAYK.), WITH DESCRIPTIONS OF THE HITHERTO UNKNOWN LARVAL AND PUPAL STAGES.

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(Plates XV–XIX.)

[Read February 28. Published April 13, 1922.]

1.—Introduction.

Nearly one hundred years ago the flax crop in parts of Ulster was almost completely destroyed while in the seedling stage as a result of the ravages of the small, black, jumping beetle, now known as the flax flea-beetle. During various intervening seasons damage due to the same cause has occurred in many parts of Ireland, and this beetle is now regarded as being by far the most dangerous insect enemy of flax, and one capable of causing losses amounting to many thousands of pounds sterling in a single season.

Like the other members of the family Chrysomelidae, it is herbivorous, feeding in the adult stage on the cotyledons and young leafy shoots of flax seedlings. The destruction of the young plants gives rise to thin, uneven brairds, and the ultimate production of dwarfed, branched, and uneconomic crops of flax; indeed, it is frequently the case that the young seedlings are entirely destroyed and large areas are laid bare, thus necessitating re-sowing.

Flax-growers have long been familiar with the ravages of this pest, which is popularly known as the "fly" or "flea"; but, despite this fact, little work has been done regarding its biology and habits, or possible remedial measures, while no details are available in entomological literature with reference to the general relations of the adult beetles and their larvae with the food plants and the soil in which the latter are growing.

In July, 1920, the writer commenced, at the Department's Field Laboratory for Flax Diseases, Coleraine, Co. Derry, an investigation on the life-history, habits, etc., of the insect, with a view to the possibility of evolving a suitable check on its ravages; and a general account of the progress made that season is incorporated in the second Report of Investigations on Flax

Diseases, published by the Department of Agriculture and Technical Instruction for Ireland (51)[1] in 1921.

The work was continued at Coleraine during the spring and summer of 1921, and in the present paper it is proposed to give an account of the life-history and habits of the beetle, together with detailed descriptions of the morphology of the different immature stages, and general information relating to the species in so far as it has been investigated up to the present.

The writer wishes here to acknowledge his indebtedness to Professor G. H. Carpenter, of the Royal College of Science, under whose guidance the work has been carried out, for much valuable help and criticism, especially with reference to the descriptions of the different stages.

2.—History and Synonymy of the Species.

The nomenclature of the flax flea-beetle has, unfortunately, been the subject of much controversy, and many descriptions under many different names have been published. Late workers, however, are agreed that the correct name of the species is *Longitarsus parvulus*—an agreement shared by the present writer.

From 1762, when Geoffroy (26) proposed for the flea-beetles the generic name *Altica*, until 1807, when Illiger (37) divided his genus *Haltica* into nine sections, and defined the characters common to each section, the position of the group was conjectural. Illiger gave to the seventh section the name "Longitarses"; and Latreille (46), in 1829, raised this section to generic rank. Two years later Stephens (59), in a new system of classification, founded the generic name *Thyamis*, and substituted it for *Longitarsus* Latr., while a further change was made in 1834 by Chevrolat (16), who, instead of employing either *Longitarsus* or *Thyamis*, used the new name *Teinodactyla*. *Longitarsus* is, therefore, the legitimate generic name.

The specific names *parvulus* and *ater* have been used simultaneously by various authors. Patterson (48), to whom the first record of damage to flax in Ireland by the species is due, uses the former, while several years later Janson refers specimens from Irish flax fields to the same species (61). After the publication of the catalogue of Gemminger and Harold (25), in which *ater* is given priority (from *Altica atra* F.), many writers adopted the latter specific name. Thus, it has been used by Bargagli (2) in Italy; Fowler (24), Sharp and Fowler (58), Hudson-Beare and Donisthorpe (36), and others in England; and Johnson and Halbert (39) and Carpenter (8) in Ireland.

[1] The numbers in brackets refer to the literature cited.

In 1775 Fabricius (19) described *Altica atra* thus:—"A. atra, nitida, antennarum basi plantisque piceis . . . parva, tota atra, solis plantis pedum et basi antennarum subrufescentibus," with a reference to the *Altise 8* of Geoffroy (26). Twelve years later the same author (20), using a new system of classification, gives to *Chrysomela atra* a similar description; while in 1792 (21) he adopts the generic name *Galleruca*, and under *G. atra* is the description:—"G. saltatoria atra nitida antennarum basi pedibusque piceis . . . . parva tota atra solis pedibus piceis," with references to *Chrysomela atra* F. and *Altise 8* Geoff. Paykull in 1798 (50) further described a species as *Galeruca atra*, having *G. atra* F., and *Altise 8* Geoff. as synonyms.

In 1801 Fabricius (22) again altered the classification; substituted the name *Crioceris atra* for his *Galleruca atra*, and gave the latter, *G. atra* Payk., and *Altise 8* Geoff., as synonyms. In all Fabricius' works *atra* appears either immediately before or after *nemorum*—our present *Phyllotreta nemorum*.

Subsequent authors are not agreed that *Altica atra* F., *Chrysomela atra* F., *Galleruca atra* F., *Galeruca atra* Payk., and *Crioceris atra* F. are identical. Thus Gyllenhal (27) gives *Crioceris atra* F. as a synonym of *Haltica parvula* E. H.; Hoffmann et al. (33), Duftschmidt (18), and Redtenbacher (52) refer *Crioceris atra* F. to *Haltica atra*; while Olivier and Illiger (37) regard it as a synonym of their *Haltica atra*, which would appear to be different from the *H. atra* of other authors, inasmuch as it is placed by Illiger in his "Longitarses" division, being regarded by him as very like *H. anchusae* = *Longitarsus anchusae*. It may have been identical with that species. Foudras (23) and Allard (1) give *Galeruca atra* Payk., *Haltica atra* Ent. Hefte and Gyll. as synonyms of *Phyllotreta atra*, while Kutschera (44) gives *Galeruca atra* Payk. and *Phyllotreta atra* Foudras and Allard as synonyms of his *Haltica atra*. It is difficult, if not impossible, to refer definitely *Altica atra* F., *Galleruca atra* F., *Chrysomela atra* F., *Galeruca atra* Payk., and *Crioceris atra* F. to a present-day species; but from the references given it is concluded that they were our present *Phyllotreta atra*, so that the *ater* of Gemminger and Harold cannot be retained as the specific name of the species injurious to flax.

Paykull (49) in 1798 gave a description of a new species under the name *Galeruca parvula*. This description agrees precisely with the characters of the flax flea-beetle, and is that now generally regarded as the original; so *Longitarsus parvulus* Payk. is the legitimate name according to the present system of classification.

Hoffmann and his collaborators in 1803 (32) redescribed *Galeruca parvula* Payk. as *Haltica parvula*, with the former as the only synonym. Four years later Illiger (37) gave a further description under the name *Haltica pumila*,

with *H. parvula* Ent. Hefte and *Gal. parvula* Payk. as synonyms. Schönherr (57) gives many synonyms, but some of them can be referred to other present-day species. Thus, according to this author, *H. parvula* E. H., *Gal. parvula* Payk., *Crioceris atra* F., *Galleruca atra* F., *Altica atra* F., and *Chrysomela pulex* Schr. are identical.

Stephens (59), after the erection of his new genus *Thyamis*, described *Galeruca parvula* Payk. under the name *Th. parvula*, with *H. parvula* Ent. Hefte as the only synonym. After this the literature, especially British, contains many references to *Th. parvula* Steph. Thus, Curtis in 1837 (15) uses this name; Waterhouse in 1868 (62) sent the species thus named to Kutschera at Vienna, and the latter confirmed the determination; while Janson gave this name to flax-eating specimens from Ulster (61). Redtenbacher (52) was the first to adopt the combination *Longitarsus parvulus*, while Foudras (23), using the generic name *Teinodactyla* Chevr., with *parvula* for specific description, includes *H. parvula* Ent. Hefte, *H. pumila* Illig., *Th. parvula* Steph., and *L. parvulus* Redt. as the synonyms. Allard (1) in 1860 also uses *Teinodactyla parvula*; but here again *Chrysomela atra* F. is given as one of the synonyms. Two years later the binomial *L. parvulus* is again revived by Kutschera (44), with *Gal. parvula* Payk., *H. parvula* E. H., *Th. parvula* Steph., *Teinodactyla parvula* Foudr., and *H. pumila* Illig. as synonyms. In the latest European catalogue (31) *Longitarsus parvulus* is retained as the priority name, with *pumilus* Illig. and *ater* Leesb. as synonyms. Tomlin and Sharp in 1911 (60) also employ the specific name *parvulus*, while in the latest work on the species (1913) to which the writer has had access (28) a similar name is employed.

The synonymy of the species is therefore:—

Longitarsus parvulus (Payk.).

Galeruca parvula, .	Payk., Faun. Suec. ii (1798), p. 102. 22.	
Haltica parvula, .	Ent. Hefte, ii (1803), p. 59. 35.—Gyll., Ins. Suec. I, iii (1813), pp. 526–7.—Schönh., Synon. Ins. ii (1808), p. 312. 72.—Dftsch., Faun. Aust. iii, p. 268. 36.	
Haltica pumila, .	Illig., Mag. f. Insk. vi (1807), p. 170. 138.	
Galleruca atra, .	Fab., Mant. i, p. 78. 148.	Schönh., Synom. Ins. ii, (1808), p. 312. 72.
Crioceris atra, .	Fab., Sys. El. 1, p. 467. 88. Illig., Mag. i, p. 421. 88.	
Altica atra, . .	Fab., Sys. Ent., p. 115. 21.	
Chrysomela pulex, .	Schrank En. Ins., p. 85. 160.	

Crioceris atra, . Fab., Sys. El. 1, p. 467. 88.—Gyll., Ins. Suec. iii (1813), p. 526.—Allard, Ann. Soc. Ent. Fr. 3, viii (1860), p. 99.—Redtenb., Faun. Aust. (1858), p. 943.

Chrysomela atra, . Allard, Ann. Soc. Ent. Fr. 3, viii (1860), p. 99.

Thyamis parvula, . Steph., Illus. Br. Ent. iv (1831), p. 317.—Mn. 298, 2344.

Teindactyla parvula, Foud., Ann. Soc. Linn. Lyon, vi (1859), p. 258. 12.—Allard, Ann. Soc. Ent. Fr. 3, viii (1860), p. 99.

Longitarsus ater, . Gemm. and Harold, Cat. Col. xii (1876), p. 3502.—Bargagli, Bull. del. Soc Ent. Ital. x (1878), p. 73.—Sharp and Fowler, Cat. Br. Col. (1893), p. 30.—Johns. and Halb., Beetles of Ireland, Proc. R.I.A., 3, vi (1901), pp. 766-767.—Carpent. Econ. Proc. R.D.S., i, 3 (1902), p. 152.—Id., ii. 6 (1913), p. 83.—Leesb., Tijdschr., 25, p. 162.

Longitarsus parvulus, Redtenb., Faun. Aust. Ed. i, p. 535, ed. ii (1858), p. 943.—Bach. Kf. Fr. f. N. u. M., Stschl. iii., p. 149. 8.—Heyd., Reitter and Weise, Cat. Col. Eur. (1906), p. 578.—Schaum., Catal. Coleop. Eur. (1862), p. 113.—Tomlin and Sharp., Ent. M.M., 47 (1911), pp. 241–250.—Carpent., E. Proc. R.D.S., ii, 12 (1916), p. 226.—Kutsch., Wien. Ent. Monats. 7, vi (1862), pp. 223–4.—Heikert., In. Reitt. Faun. Germ. iv (1913), p. 198.

3.—Identification of the Species.

Longitarsus parvulus Payk. has long been familiar in the adult stage to Coleopterists in Ireland and Europe generally. Specimens bred at Coleraine and others received from Co. Cork were identified by Mr. J. N. Halbert, of the National Museum, Dublin; while on another occasion Mr. G. K. Blair, of the Natural History Museum, London, named specimens submitted for identification.

The other species of *Longitarsus* found in association with *parvulus* in Co. Derry were *luridus* Scop., *atricillus* Linn., *melanocephalus* De G., *suturalis* Marsh., and *jacobea* Waterh. Other species of flea-beetles, principally *Plectroscelis concinna* Marsh., *Phyllotreta nemorum* Linn., and *Sphaeroderma testacea* Panz., were also to be found on or near flax plots, but neither they nor the other species of *Longitarsus* could ever be seen attacking the seedlings.

The determinations of the above species were also made by Messrs. Halbert and Blair, to both of whom the writer acknowledges his indebtedness.

4.—Distribution.

Longitarsus parvulus appears to be widely distributed. The original description was made from specimens taken in Westrogothia (Sweden). Illiger (87) records it from the Rhine provinces, Portugal, and Sweden. According to Bargagli (2), it is common in the whole of Europe. Fowler (24) gives the British and Irish distribution thus:—"Very local; London district, rare, Chatham, Dulwich; Whitstable; Birchington; Deal; Ditchingham, near Bungay, Suffolk, abundant (Power); Ashwicken and Wicken Fen; Markfield, Leicester; Portsmouth district; Seaton Down, Devon; Ireland, Rathkurby, near Waterford (Power); Belfast (Haliday) and Armagh (Johnson)." Johnson and Halbert (39) give the distribution in Ireland as follows:—Donegal and Derry: Foyle district; Antrim: Ballycastle, Lisburn; Down: near Belfast; Armagh: Poyntzpass; Cavan: Ballyhaise; Waterford.

It is thus seen that the known range of the species in Ireland was at that time (1901) confined to the province of Ulster, with a single record from Munster. In the meantime, further records have been obtained from these two provinces, but as yet no specimens of the species would appear to have been taken in Leinster or Connaught. This may be due to the non-occurrence of the species as a pest, or, perhaps, to the absence of collectors, since it is readily conceivable that if flax were to be grown in north-west Co. Louth, it would be attacked like that grown in south Co. Armagh and south-west Co. Down. Of late years the species has become so prevalent in the flax-growing districts of Co. Cork as to constitute a serious pest, although Johnson and Halbert give no record from that county. In September, 1921, the writer took an opportunity of visiting a flax-growing district in Leinster (Co. Wexford), and made a search for flax-beetles, but without success.

5.—Description and Habits of the Adult.

The adult has been studied by many systematic workers on the Coleoptera, and representative descriptions are given in various publications (24) (60); hence a detailed description is not considered necessary here. An enlarged drawing of the adult is, however, shown in the figure A.

Except immediately prior to egg-laying, the sexes can hardly be distinguished at sight. The gravid females are, however, quite distinct from the males, as the abdomen is distended ventrally and posteriorly, so that the elytra do not completely cover it, but appear somewhat convex. Moreover,

the tergites and sternites of the abdominal segments are pushed apart, so that they appear as black bands in the yellow intersegmental cuticle. The aedeagus of the male, as shown in the text figure B, is a conspicuous, elongated, and strongly chitinized organ, which normally remains retracted into the abdomen. Slight pressure will, however, cause its protrusion, and then the sex can be determined.

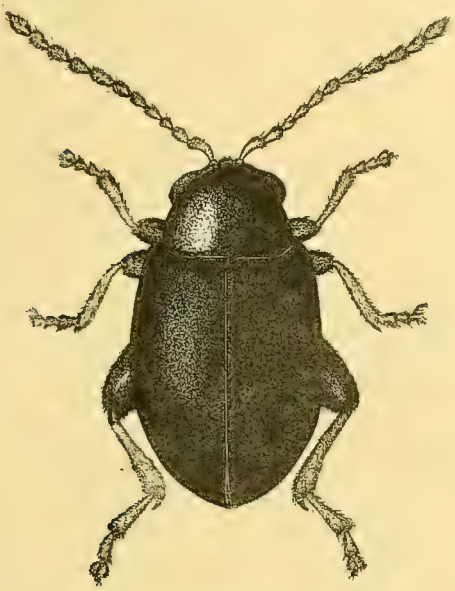

Fig. A.
Longitarsus parvulus.
Adult. × 26.

Fig. B.
Aedeagus of Male.
× 86.

The beetles are most active, and are seen in greatest numbers during sunny weather, especially during bright sun after showers of rain. In wet weather they are not noticeable, as they are then in the soil, sheltering beneath little lumps of earth. But when the rain ceases and sunshine supervenes, they come up and rest on dry stones in the soil, or even on lumps of soil, prior to ascending the food plant. When the top of the plant is reached, suitable leaves are selected, and feeding commences. Thus the youngest foliage is always selected for food, and rarely does one find a beetle feeding on foliage low down on the plant. The beetles appear to favour the thinner parts of a braird, and to eat the seedlings on such parts in patches, so that thin, uneven brairds of weakly seedlings are most liable to be attacked. Flight is common in spring, when the adults leave their winter quarters to go to fields of flax, and again towards the end of the season, when the crop has been pulled. During the active feeding period flight rarely occurs, as the beetles

move about chiefly by jumping, although walking with the ungainly gait characteristic of flea-beetles is also common.

The adults of this species possess extraordinary jumping powers, and are extremely difficult to catch during warm weather in May and early June. They are much more active than the related turnip flea-beetle, and more sensitive to approaching disturbances. This activity wanes as July approaches, as by that time the life of these adults is practically at an end. When not feeding, the beetles often shelter underneath the leaves of flax plants, where they are hidden from the casual observer.

6.—Occurrence as a Pest.

The first mention of the species from the economic point of view appears to have been made by Patterson, of Belfast (48), who thus describes its ravages: "As linen is the staple manufacture of this part of the country, and gives employment in various departments to many thousand persons, the flax crop is naturally regarded as one of very high importance; yet here a diminutive insect had the hardihood to interfere, and, despite of all the efforts of man, nearly destroyed in many parts of the Co. Down, in the summer of 1827, the entire crop of flax. The minute assailant was a little jumping beetle (*Haltica parvula*), resembling that called the turnip-fly, but much smaller."

The next record of damage is found in the *Transactions* of the Entomological Society of London for the year 1869 (61), and is to the effect that the Secretary of the Society "read a letter from the Secretary of the Flax Improvement Association of Belfast, respecting the damage done by a small beetle to the flax crop, especially whilst the plant was in the seed leaf. The species was determined by Mr. Janson to be the *Thyamis parvula* of Paykull."

Under the name *Longitarsus ater* Fab., Carpenter (8) records an attack near Lisburn in June, 1901, and mentions that the insects had eaten nicks and holes in the young, tender leaves. This is presumably the same attack that is referred to in the *Journal* of the Department of Agriculture and Technical Instruction for Ireland, 1901 (40), in a report on a sample of flax plants sent from Lisburn which were found to be attacked by *Longitarsus ater* Fab., and "holes and nicks had been eaten out of the leaves of the opening leaf-buds." Further ravages of this pest are recorded by Carpenter in his report for the year 1912 (9). During that season the beetles appear to have been very numerous and destructive, some fields having the brairds completely eaten in patches, and not a single plant left; whilst in parts of Co. Antrim the crop had to be resown. A further report by Carpenter (10) is to the

effect that "in June, 1915, it was particularly abundant and destructive in Ulster"; and in his latest report (11) he mentions that "this destructive little beetle caused much damage to the flax crop in all three seasons under review"—1916, 1917, and 1918—and that "in 1917 and 1918 it was found necessary to resow the crop in several localities." It has been estimated that in the year 1917 fully 30 per cent. of the early sown flax in Co. Down was destroyed by flax flea-beetle attacks.

In the reports of the manurial experiments on flax carried out by the Department of Agriculture, two instances of insect attack are mentioned which, although obscure, may with tolerable certainty be referred to the flax flea-beetle. In the report of the 1909 season experiments (41), when referring to factors affecting the growth of the crop, a statement is made to the effect that "at Ballindrait the brairds were badly eaten by grub"; and the report for season 1913 (42) states that at Newmills centre, "after the brairds suffered injury from an insect attack, the crop grew so irregularly as to render necessary the abandonment of the trials." The latter is obviously a reference to flea-beetle injury; but, in the first case, the damage may have been caused by "leather-jacket" grubs (*Tipula* sp.). During the season of 1919 severe attacks were reported from the flax-growing districts of Co. Cork, and in Ulster the species was abundant, and did appreciable damage.

The season of 1921 was remarkable because of the long drought—a condition often suggested as most favourable to the ravages of flea-beetles—yet during that season the flax brairds of the different districts in Ireland where the crop is grown were singularly free from attack, and few reports of serious damage have been recorded.

From Ballinacurra, Co. Cork, a complaint was received that some early sown plots of flax at the Department's plant-breeding station there were being injured by insects, and on examination of the specimens forwarded the species was identified as *Longitarsus parvulus* Payk. The attack was, however, local and chiefly confined to very early sown plots. A similar condition prevailed at the experimental plots in connexion with the field laboratory in Co. Derry. A series of plots sown early in April, and brairding during the last week of that month, were extensively infested, and the young plants suffered considerably. The remainder of the plots were sown during the first week of May, and, brairding twelve days later, were not so attacked, and suffered little appreciable injury, although beetles were present in small numbers, having migrated thence from the earlier sown plots. During the brairding of the flax on the latter the beetles were observed flying to them from all directions; and it is possible that, as this was the only flax brairding in the immediate district, the beetles swarmed on it as

the favoured food plant, attracted thereto by tropisms as yet unexplained. Apart from these slight attacks—both of which occurred on early sown flax—the brairds of 1921 suffered little, if at all, from flax flea-beetle depredations. Some probable factors in the origin of this freedom from attack are discussed in section 9.

Outside of Ireland there are few, if any, authentic records of damage to flax by this species. Heikertinger (28) records *parvulus* as the only species of the genus *Longitarsus* known to injure flax; but there is nothing to indicate that the injury referred to occurred in Germany. More recently, Blunck (3) includes *L. parvulus* Payk. in his list of the insect and other animal enemies of flax; but here again the country is not specified. Kuhnert (43) does not make any mention of *L. parvulus*, but records *Phyllotreta nemorum*, our turnip flea-beetle, as destructive to flax seedlings.

7.—Range of Food Plants.

Cultivated flax, *Linum usitatissimum* L. is, undoubtedly, the favoured food plant, and is eaten in preference to all others, with the possible exception of narrow-leaved flax, *Linum angustifolium* (Huds.). The latter is a dwarf spreading species, found growing wild in the south and east of Ireland, but not in the north. A small plot grown from seed at Coleraine in 1920 became badly infested with beetles, and was eaten simultaneously with cultivated flax growing alongside. The preference for flax is well seen in spring if a small plot be sown early. The beetles, if the weather be suitable, will gather to it rapidly and feed voraciously, showing no desire for other plants. Purging flax, *Linum catharticum* L., is eaten if supplied to beetles in captivity; no definite proof, however, of its having been eaten in the open could be seen.

Other alternative food plants are clovers and grasses. These have been observed to be eaten both in the field and in laboratory cages; but in the open are only attacked late in the year after the flax has been pulled, and possibly in spring, if there is a spell of dry warm weather before the flax brairds are ready. Twenty beetles lived happily on a plant of white clover (*Trifolium repens*) in one of the laboratory cages. The leaflets were not notched or perforated, but were eaten from the under surface, usually near the insertion of their stalks, the upper epidermis being left intact. In the field, however, leaflets with notches eaten out have been observed late in the season. Of the grasses, the younger leaves seem to be preferred.

Some experiments were made to determine if the beetles showed a preference for any of the common weeds when flax is not available.

Seedlings of various weeds were raised in pots, and a number of adults caged on each species of weed, no other food being supplied. The following weeds were used:—Spurrey (*Spergula arvensis*), Daisy (*Bellis perennis*), Dock (*Rumex* sp.), cut-leaved Geranium (*Geranium dissectum*), Goosefoot (*Chenopodium album*), Charlock (*Sinapis arvensis*), and Redshank (*Polygonum Persicaria*). In all cases the seedlings remained free from attack, the beetles showing no attempt to feed on them. In the field, observations were made to detect, if possible, weeds eaten by the beetles, but no definite instance of such could be seen.

Records of food plants in the writings of other workers are singularly rare, and, beyond these from flax in Ireland, there is little definite information to be found. Allard, according to Fowler and other writers, states it is commonly found on the Hornbeam (*Carpinus Betulus*) in woods ; but that it actually feeds thereon is doubted by some authorities. The present writer has not had an opportunity of making observations regarding this possible food plant. "On low plants" is the general habitat given by Fowler (24), whilst the original description gives the "habitat in pratis ad fossas in Westrogothia Dom. Gyllenhal" (49), but mentions no food plant.

8.—Nature of Damage.

(*a*) *By the Adult.*—The principal damage is caused to the flax in its seedling stage, and by the adult insect. The cotyledons of the seedlings are the parts first attacked, with the result that they become perforated and notched, as shown in Pl. XV, figs. 1, 2, 3. If the attack is severe, the entire cotyledons and the terminal bud between them may be devoured, in which case the seedling succumbs.

When this is not the case, and when the terminal bud proceeds to give rise to young foliage leaves, the beetles leave the cotyledons and begin to devour these tender leaves. Even at this stage the severity of attack may increase, so that the young plant becomes entirely destroyed.

It frequently happens, however, that the attacked seedling goes on growing and ultimately produces a plant. Nevertheless, the injury done to the terminal bud of the seedling induces the development of lateral buds in the axils of the foliage leaves which would otherwise remain dormant, hence flax plants which in their early days have been attacked by the flea-beetle are frequently branched, but such induced branching must not be confused with the normal branching which is found in some strains of cultivated flax.

It is noticeable that the beetles always prefer the newly developed foliage leaves ; and at a given time they are nearly all to be found in relatively the

same regions of the plants, the most favoured one being between two of the newly developed leaves just behind the growing point. The effects of the feeding beetles become less obvious as the plants increase in size, and little anxiety is felt regarding damage. The newly emerged adults in August attack old flax stalks, and have been observed to "bark" them completely in the attempt to secure sufficient preferred food.

(*b*) *By the Larva.*—The feeding larvae live on the flax roots, tunnelling into and feeding upon their soft parenchymatous tissues. The youngest parts of the roots seem to be preferred. Whilst plants growing in restricted amounts of soil in pots in laboratory cages suffered as a result of the larvae feeding upon their roots, no damage which could be ascribed to the activities of feeding larvae was observed in seedlings growing in field cages, or in plots in the open field. This is probably due to the fact that about three weeks must elapse from the time the eggs are laid until the larvae are capable of doing appreciable damage, and during this time the flax plants will have formed an extensive root system, and thereby become proof against serious injury. The fact, however, must not be overlooked, that where the growth of seedlings has been delayed, owing to unsuitable conditions, or otherwise, the inherent possibility of these larvae feeding in the roots, and thus further retarding growth, always remains.

It is interesting to note that in the case of the larvae of the Chrysomelid genus *Donacia*, which live upon the roots and stems of aquatic plants, Böving (4) concludes that the plants rarely suffer from the effects of the feeding larvae. Howard (35), referring to the larvae of the tobacco flea-beetle (*Epitrix parvula F.*), which feed upon the roots of the tobacco plant, is of opinion that "the damage done to the roots . . . must affect the health of the plant to a certain extent, but it is not appreciable in comparison with the damage which the adult beetles do to the leaves." Chittenden and Marsh (14) state that the injury done to cruciferous plants by the root-feeding larvae of the Western Cabbage Flea-beetle (*Phyllotreta pusilla* Horn.) is negligible, but the larvae of the Desert Corn Flea-beetle (*Chaetocnema ectypa* Horn.) are, according to Wildermuth (63), highly destructive to alfalfa and maize by reason of the damage done to the roots on which they feed.

9.—Conditions which Favour Attacks.

The opinion is generally held by farmers that attacks by flea-beetles are largely governed by the time of sowing, tilth of soil in the seed-bed, and the prevailing weather conditions at and for weeks after brairding—all factors which tend to exert considerable influence on the rate of growth. Thus,

given dry, warm weather in May, after weather not conducive to the thorough cultivation of the seed-bed, the prospect of a bad attack becomes highly probable, inasmuch as such conditions retard the growth of the seedlings at a time when, stimulated by the prevailing warmth, the adult beetles are encouraged to come out of hibernation; whereas if the weather remains cold, although growth may be seriously checked, the beetles are not encouraged to activity, and therefore the seedlings escape their attentions. When, however, conditions conducive to vigorous growth are secured, the dangers of serious results from attack are minimized, because the seedlings are enabled by rapid growth to overcome the possible effects.

Early sown fields often suffer considerably greater damage than those sown some days later. This was very apparent in Co. Down about four seasons ago, when many growers had the brairds on the early sown fields completely destroyed, although later sown fields suffered much less, and the latest ones were not appreciably damaged. The reason for this is not yet clear, but, as already pointed out, the beetles gather in, probably attracted by a scent stimulus, from surrounding hibernating places to a field in which flax is brairding. Since brairding flax is not common at this early period, it is highly probable that all the beetles which have hibernated in that particular district will come to the young seedlings. Moreover, the beetles have a greater capacity for food after coming out of hibernation, and prior to egg-laying, than at a later period, so that a field of early sown flax is attacked by a much greater number of beetles which, individually, possess the maximum capacity for food.

The idea that warm, dry weather favours a bad attack only holds provided the beetles are actually present to cause the injury. Thus, the season of 1921 was an ideal one as regards suitable weather for flea-beetle depredations; nevertheless, as already stated, there was an uncommonly slight infestation throughout the different districts. From the study of the life-history and observations thereon, the writer is of opinion that the prevailing weather during May and June, i.e., the months during which the earlier stages are passed, determines to a large extent the infestation of the *following* spring; because it is the beetles which emerge during late July and August as a result of eggs laid in May that are, after the hibernation period, responsible for the damage which may be caused during the following season. Therefore, if the weather during the months of May and June is fine, dry, and otherwise conducive to the health and safety of the minute and delicate larvae in the soil, the number of adults ready to attack flax seedlings the following spring will be correspondingly large. Moreover, if warm, sunny weather prevails during late April and early May, the females

are induced to oviposit early, and a correspondingly early emergence of a brood of adults will result.

This early emergence further helps in the multiplication of the species, because it is completed before the pulling of the flax crop begins, and the soft, delicate pupae in the soil will thereby escape possible injury and destruction during the process. The weather during the hibernating period and the convenient presence of suitable and reliable winter quarters are also factors which undoubtedly influence to a large extent ultimate infestation.

The season of 1920 was particularly wet and cold, with little sun during the early part of May. Egg-laying was consequently delayed, and the emergence of the resulting brood of adults had only commenced when the pulling of the flax crop started. The pupae were present in the soil in considerable numbers, and no doubt many were destroyed, and others injured sufficiently to prevent emergence of the adults. The mortality would be further increased by the subsequent operations, such as carting, and further by stock grazing on the fields after the flax had been removed.

Besides these checks on emergence, the wet, cold soil must have caused a comparatively high death-rate amongst the newly hatched larvae, as actually occurred in the rearing experiments conducted in laboratory cages, when the soil in which the supporting seedlings were grown was watered to excess.

These adverse conditions may, therefore, have been responsible for the singular freedom from attack last season (1921), and, if so, we may anticipate bad infestations during seasons following a dry and warm spring and summer. In this connexion it is interesting to note that Carpenter, when recording the unusually destructive attacks of May, 1912, states that such were "probably as a result of the hot and dry summer of 1911" (9).

10.—Descriptions of the Immature Stages.

(*a*) *The Egg* (Pl. XVI, fig. 6). — Elongate, oval in shape, cylindrical, with rounded ends; where two or more are pressed together in a cluster, the sides sustaining the pressure are sometimes flattened. The chorion is tough, and under high magnification is seen to be covered with numerous depressions, which are bounded by more or less straight five-, six-, or seven-sided walls, the raised areas between the depressions giving to the surface a distinct and characteristic network appearance (Pl. XVI, fig. 7). After oviposition, the colour is pale yellow, and the surface appears shining and translucent; during hatching the colour changes to yellow-brown or orange, and the surface becomes opaque and dull. Eggs which have been deposited for eight or nine days show up in fairly striking contrast to the soil in which they are deposited.

The average length is 0·59 mm. and the average greatest breadth 0·23 mm. The size is, however, not uniform, as the following measurements of eggs from different clusters show:—

Length (mm.)	Greatest Breadth (mm.)
0·55	0·17
0·61	0·23
0·61	0·28
0·64	0·29
0·55	0·20
0·58	0·21

(*b*) *The fully grown Larva* (Pl. XVII, fig. 23).—The details of the larval descriptions which follow are from fully grown specimens, and to avoid repetition the description of the fully grown larva is placed before those of the earlier stages.

The length varies from 3·6 mm. to 4·5 mm., according to the time that had elapsed since the previous moult. Form narrowly elongate, nearly cylindrical, the sides more or less parallel from the posterior margin of the prothorax to the posterior margin of the eighth abdominal segment, the average diameter being 0·40 mm. Colour opaque white, excepting for the head and the posterior end of the abdomen (ninth abdominal tergum), which are firmly chitinised and of a dark orange-yellow colour. The cuticle otherwise is soft throughout, and bears numerous brown coloured bristles on indistinct tubercles, which are placed on the body in a regular order.

(i) *Head* (Pl. XVIII, figs. 25, 26, 27).—This consists of a strongly chitinised capsule, which completely envelops the dorsal and lateral regions. Ventrally, the head is feebly chitinised and white in colour. The chitinous part is dark yellow or orange, and when viewed from above with a low-power binocular is seen to be divided into two distinct parts by a narrow dark ridge, which extends along the median line. The capsule is strongly arched towards the posterior margin, and the latter is hollowed out into a deep V-shaped groove. From the centre of the groove the epicranial suture (*epsu*) extends anteriorly, and appears as a light-coloured narrow space for a short distance along the median line. It then divides to form the two frontal sutures (*frs.*), which extend obliquely forward and outward to become obsolete a short distance from the margin of the frons at the insertion of the antennae. These sutures also appear as clear lines in the chitinous capsule, and together form a well-defined V, enclosing the portion of the head known as the frons. The frons (*fr.*) is divided into two by the dark brown or black

line already referred to, which extends from the junction of the epicranial and frontal sutures along the median line to the epistome. This is the frontal ridge (*frr.*), and is obviously a strengthening band of chitin. The dorsal surface of the head is therefore divided into three distinct areas :—the epicranial region (*epc.*) at each side, and the frons. The epicranium extends ventrally to the fleshy stipes of the maxilla, and supports the antenna laterally and towards the anterior margin.

The frons is sub-triangular, and has along its anterior margin a very strongly chitinised narrow region—the epistome. The latter is emarginate anteriorly for the clypeus (*cl.*), and extends laterally to the pleurostome (*pls.*), which provides, on its anterior margin, articulatory surfaces for the condyles of the mandibles. The clypeus is a narrow transverse band, extending between the epistome and the labrum. It is little chitinised, and pale yellow in cleared preparations. Anteriorly it is emarginate for the labrum, the posterior margin of which is situated ventral to the clypeus, so that normally the articulation for the labrum is along the ventral surface of the anterior margin (Pl. XVIII, fig. 34). The ventral surface of the head (Pl. XVIII, fig. 25) shows the fleshy protruding maxillae, between which is the globular submentum (*sm.*) of the labium. Posterior to the submentum is a membranous region, little chitinised, which corresponds to the gula (*gu.*). Between it and the prothorax there is no distinct suture, and it may therefore be regarded as an anterior extension of the prothorax.

The maxillary and labial palps project antero-ventrally, and the mandibles cross beneath the labrum, so that normally none of the mouth-parts except the labrum is visible in dorsal view.

The study of the arrangement of the bristles (setae of many writers) on the head-capsule is important, for, as already pointed out by workers on Lepidopterous larvae, they may prove to be highly useful in the differentiation of closely allied species (29). Generally speaking, the head bristles on *L. parvulus* larvae are in transverse rows, somewhat similar to those on the body, to be described later. Each lateral region of the epicranium carries on the dorsum two pairs of strong bristles, one pair being beside the frontal suture and the other towards the lateral margin. Slightly anterior to, and medianly from, the latter pair of bristles a round clear spot, resembling the follicle of a bristle, occurs in the chitin. Following Heinrich (29), such spots are called punctures. Towards the posterior angles of the epicranium there occurs at each side a series of five such punctures, in which very minute bristles may sometimes be seen. These occupy a somewhat similar position on the head to the ultra-posterior punctures (secondary punctures of Heinrich) described for various species of Lepidopterous larvae (7), (30),

(34). Midway between the two large bristles, which occur near the frontal suture at each side, there is a minute puncture, which sometimes carries a more minute bristle. Just ventral to the lateral margin of the epicranium another strong bristle occurs, and antero-ventral to it is a puncture. Ventral to the antenna there is anteriorly and near the pleurostomal margin a strong bristle, whilst a small one arises ventral to and near the posterior extremity of the insertion of the first antennal segment.

The frons carries a transverse row of four long, strong bristles, which arise just on the posterior margin of the epistome. Posteriorly, and in the order given, there are present also on the frons two small bristles (one at each side of the frontal ridge), two punctures, and, well back towards the epicranial suture, two further punctures.

The close similarity between this arrangement of bristles and punctures and that commonly found on the head capsule of Lepidopterous larvae is very apparent, and is here referred to because of the interest which such similarity affords from the phylogenic point of view.

The clypeus is provided with a transverse row of what appear to be bristle-follicles or punctures, but close examination reveals very minute bristles in them (Pl. XVIII, fig. 35). The number does not appear to be constant; four at each side is the usual condition, although an additional one is often present at either side.

The antennae (Pl. XVIII, fig. 28) are situated on the lateral margins of the epicranium, and just posterior to the pleurostome. Each consists of three segments,[1] the basal one being large, flattened, and in close contact with the head. The middle segment is smaller, more cylindrical, and is provided with a number of sensory structures towards the apex. These consist of:—a long, blunt, prominent process, which arises on the inside of the segment, and projects inwards and forwards; three short and blunt spines, which arise from rounded pits; and one or two similar pits devoid of such spines. All these structures are on the dorsal aspect of the segment. The terminal segment is sub-conical, inclined to be somewhat pear-shaped, and is not provided with any sensory appendages.

Ocelli are absent.

(ii) *Mouth parts.*—The labrum (Pl. XVIII, fig. 34) is light yellow in cleared preparations, and somewhat triangular in shape. The free margin is distinctly tripartite and arched dorso-ventrally. Each outer lobe carries five strong blunt bristles, which arise from the ventral surface near the margin, and curve inwards towards the centre, while the middle lobe is provided

[1] Some writers regard the flat basal segment as a projection from the head. In this paper it is considered a distinct segment.

with two series of short, straight projections, also from the ventral surface of the margin. Dorsally there is a transverse row of four long bristles, one from each of the lateral angles being much longer than the median pair. Between the latter there are two round and comparatively large punctures.

The epipharynx (Pl. XVIII, fig. 36) is closely attached to the ventral surface of the labrum, and often difficult to define. It would appear to be a membranous structure, having a series of four short, blunt projections at each side of a somewhat triangular concave area.

The mandible (Pl. XVIII, figs. 29 and 30) is strong, firmly chitinised, dark brown or black, prominently situated ventral to the labrum. The base is roughly triangular in section, and the apex is divided into five strong blunt teeth. From the ventral posterior angle a prominent condyle arises, which articulates with the head capsule by means of an acetabulum formed in the ventral anterior angle of the pleurostome. Dorsal to the condyle is the insertion of the abductor muscle, whilst the much stronger adductor is attached to the inner surface of the dorsal posterior angle.

The mandible is strongly arched, and carries on the outside towards the posterior margin two small bristles. The molar region is provided with two sharp, stout spines, which project inwards towards the buccal cavity. The anterior spine is larger and distinctly curved.

The maxilla (Pl. XVIII, figs. 31, 33) is prominent by reason of the fleshy stipes and projecting palps. It consists of galea (*gal.*) and lacinia (*lac.*) imperfectly divided; palp (*mp.*), supported by a large palpifer (*pfm.*); large stipes (*st.*); and small basal cardo (*c.*). The cardo is soft and little chitinised, roughly rectangular, and has a process for articulation with the head at the outside basal angle. It bears a single minute bristle towards the lateral margin and posterior to the cardo-stipes joint. The stipes is strengthened by a pronounced band of chitin, which extends anteriorly to encircle the lacinial region on the inside. It carries one large and one small bristle, between which is a single puncture. The galea is rounded and strengthened by a chitinous band, which encircles the apex. The latter carries a number of short, blunt spines, and one larger, two-segmented spine.

On the ventral surface of the galea and slightly below the apex three minute bristles occur, the innermost being longest, and placed on or near the lacinial region. The lacinia cannot be separated from the galea. It consists of a narrow band of tissue, from which there arise on the ventral face and near the apex five long, slender bristles. These project inwards, and normally are in close contact with the hypopharynx. The palpifer is a stout structure, strengthened by an enveloping band of chitin. It carries two small bristles on the ventral surface, and has one round puncture just dorsal to the lateral

margin. Exhibiting all the characters of a palp segment, it supports the three-segmented maxillary palp. The basal segment of the latter is narrow, strengthened by an enveloping band of chitin, and has on the inside (dorsal) face one small bristle and two punctures. The second segment is similarly strengthened, and has one small bristle on each of the dorsal and ventral faces, and a couple of punctures dorsally. The terminal segment is subconical, not chitinised, and does not carry any bristles.

Labium (Pl. XVIII, figs. 25 and 37).—This can easily be recognized by the two short palps (*lp.*), which project ventrally and slightly forward. These are simple, unsegmented structures, without any sensory appendages. They arise from short, flat, ring-shaped palpifers (*pfl.*), which are supported on a broad, rounded basal piece—the mentum (*me.*). Besides the palps, the mentum carries a pair of long bristles, which are placed near the posterior margin. It is supported by the globular and fleshy submentum (*sm.*), which extends posteriorly to occupy the middle position as far as the gula. It has two pairs of bristles, which arise near the lateral margins; one bristle at each side is anterior, and the other is situated near the posterior angle at each side.

Anterior to the mentum and intimately fused with it is a well-defined area provided with a number of minute but distinct structures. This is the remarkably modified ligula (*lig.*) or fused labial laciniae and galeae. The structures which it bears are obviously sensory organs, and no doubt are equivalent to the spines and bristles already described as occurring on the apices of the maxillary laciniae and galeae. There are five of these organs at each side of the middle line of the ligula. The two nearest the anterior margin have strongly chitinised bases, from which project pointed spines. Posterior to these are two pairs; the inner pair resemble minute cylinders, and are not provided with observable projecting spines, but the other (outer) pair have pointed processes arising from circular pits. The next pair resemble those last described, and the posterior pair are similar to those described as the inner pair of the second anterior row. In young larvae the bristles of these structures are usually longer than in fully grown larvae, while occasionally an extra organ is present at one side or the other. Fig 13, Pl. XVIII, shows the general arrangement of these structures and of the other parts of the labium. The tip of the hypopharynx is seen projecting beyond the ligula.

Hypopharynx (Pl. XVIII, figs. 32 and 37).—This is closely attached to the labium. In preparations of the complete head it is seen as a rounded prominence, occupying the greater part of the region between the mandibles immediately ventral to the opening into the buccal cavity. Under

a very high-power magnification this portion is seen to be provided with numerous slightly elevated papillae, from which there arise very minute hairs. No doubt, these are taste organs, and possibly sensory with regard to touch. These papillae extend inwardly on the dorsal face, and are present on two somewhat raised lateral areas or lobes, where, moreover, their hairs are longer. From their position and structure these lobes may represent maxillulae, which have already been described as occurring in many species of coleopterous larvae. A chitinous band extends at each side of the hypopharynx, and posteriorly forms a point of attachment for muscles for the movement of that organ.

(iii) *Thorax* (Pl. XVI, figs. 12 and 13).—The prothorax is the smallest segment, the mesothorax larger, and the metathorax largest. The pronotal shield is not strongly chitinised, and not distinct, undivided dorsally, but prescutal and scuto-scutellar areas indicated by two transverse rows of bristles; the shield has a distinct mid-dorsal suture, on each side of which three bristles occur in each of the two transverse rows. One row is placed just anterior to the posterior margin of the pronotum, while the second series of bristles arises towards the front margin. The last bristle in each series occupies a position on the raised lateral margin, which corresponds to the alar lobe.[1] This area further carries another small bristle which arises in front of the anterior series. Ventral to the alar lobe and towards the front margin a single bristle occurs on a small pigmented plate in the cuticle.

The mesothoracic and metathoracic tergites are divided into two distinct areas, the anterior one representing the prescutum and the posterior the scuto-scutellum. The mesothorax, when a cleared and stained larval cuticle is examined, shows many and variously shaped, granular-structural plates, from which arise the brown tipped bristles. These areas are present in a certain definite order on all the segments of the body, but in the case of the pronotum and ninth abdominal tergum fusion has taken place in the modification of these parts for particular purposes. They are analogous to the oftentimes very prominent and pigmented areas present on the segments of larvae of many other Chrysomelidae, e.g. *Phyllotreta nemorum*.

In *L. parvulus* larvae they are not conspicuous when living specimens are examined; in fact, if the larva has recently moulted, they are often difficult of determination, even in cleared and stained preparations. Those occurring laterally, however, appear (especially in young specimens) as prominent lobes on the pleural region of the abdominal segments one to eight. The

[1] The terminology used is adapted from Böving and Champlain: Larvae of North American Beetles of the family Cleridae. Proc. U. S. Nat. Mus., 57 (1920), pp. 575-649.

bristle-bearing areas or plates occurring on the metathorax area: a narrow, transversely elongated plate having a median longitudinal suture and provided with a single bristle at each side, on the prescutum; lateral to this plate is a small triangular-shaped one devoid of bristles; the united scuto-scutellum has dorsally a plate similar in construction and armature to that of the prescutum, while lateral to it at each side a single bristle-bearing triangular-shaped plate occurs; ventral to this and extending longitudinally across the segment is a large crescent-shaped plate, with one large bristle at the posterior end, a larger bristle medianly, and two minute bristles anteriorly. This plate occurs on the alar lobe, and the bristles on it may be referred to as the alar bristles. Ventral to the alar lobe, towards the posterior margin, is a small plate bearing a single bristle. From the position of the spiracle this may be regarded as the homologue of the plate occurring on the epipleural lobe of the abdominal segments, and its bristle is therefore the epipleural bristle of the mesothorax. Anterior to this is the plate in which the spiracle opens. It is roughly triangular in shape, and the anterior angle carries a small bristle.

On the metathorax the arrangement of the bristle-bearing plates and bristles is exactly similar. Here, however, the alar-lobe plate is larger, and the spiracular plate has not a visible spiracle, thus differing from other Chrysomelid larvae, e.g. *Donaciae*, inasmuch as the latter, according to Böving, possess on the metathorax a pair of "small, impenetrable, and useless spiracles (5).

The legs are placed latero-ventrally towards the posterior margin of the segments on prominent coxal (hypopleural) lobes. The thoracic sternites are imperfectly divided, and the different areas difficult of determination. The sternum of the prothorax has two large plates fused at the middle line and provided with one pair of fairly large bristles near the median line and towards the post-sternellum. The meso-sternum carries a pair of large fused plates anteriorly. These bear a single pair of bristles, and, towards the posterior angles, a pair of minute punctures. The post-sternellar region has a small triangular plate at each side of the median line provided with a single minute bristle. The meta-sternum is similarly strengthened and armed, but the anterior plates are usually smaller.

(iv) *Legs* (Pl. XVII, figs. 16 and 19).—These are all about equal in size, short and stout. They appear to be composed of segments homologous with the coxa, trochanter, femur, tibia, and tarsus of the adult. The coxa articulates with a large flattened, chitinised acetabulum, which is supported by the coxal lobe. Anteriorly the acetabulum is strengthened by a thick band of chitin, which passes laterally as a ridge. This is armed with usually two, but

sometimes three, long, stout bristles, while a number of smaller bristles occur on other regions of the acetabulum, as is seen from the drawings. The acetabulum, or chitinised part thereof, appears to be analogous to Sanderson's tubercle IX (56), which was considered by him to be the same as the "trochantin" described by a previous worker. The coxa is fairly large and fleshy, but not well seen from the inside, as it is obscured by the trochanter, a triangular piece which extends on the inside of the leg towards the acetabulum. At the outside the trochanter is narrow and not armed, but from the inside face one very long and a few short bristles arise. The femur is rectangular in profile, and comes off from the trochanter at an angle. It also carries on the inside one very long bristle, and towards the front a few short, stout bristles. The tibia is elongate-narrow, and is armed with many short, stumpy bristles. The tarsus is very small, and is best seen in inside view. It is closely approximated with a single, strongly chitinized, backwardly curved claw. A small bristle occurs on the inner surface near the apex. External to each claw there occurs a large, rounded bladder-like tunica (pulvillus of some writers). This shows, under a high-power magnification, a series of longitudinal wrinkles or folds, which suggest capabilities for expansion if necessary. It is obviously an organ for facilitating locomotion, and appears to be general in the larvae of flea-beetles. Carpenter[1] has described it as occurring in the larva of *Psylliodes chrysocephala* L. (12). The writer finds a similar structure well developed in the larvae of the genus *Phyllotreta*; while Sanderson (56) gives it as a specific character in the classification of Chrysomelid larvae. The similarity between this arrangement of larval foot-structures and that found in the members of the Collembola genus *Sminthurus*, as pointed out by Carpenter (12), is highly interesting in view of the recent proposal to regard the Chrysomelidae and other families of Coleoptera having specialized larvae as being primitive types (45).

(v) *The Abdomen.*—This is composed of ten segments, of which the first eight are similar regarding armature and general structure. The first is the smallest, and the eighth often the largest. Each tergum of segments one to eight is dorsally divided by transverse depressions into three distinct areas—prescutum anteriorly, scutum medianly, and scutellum posteriorly. The scutum is always the smallest of the three regions, and is very narrow on the first abdominal tergite. The prescutum bears dorsally a single transversely elongated plate, which extends unsutured across the median line, and is provided with two bristles. Lateral to this at each side, and horizontally

[1] With reference to the position of the tunica, the word "internally" occurring in the paper referred to is an error. The tunica is external in *Psylliodes*, as in *Longitarsus* and *Phyllotreta*.

opposite the alar and epipleural lobes respectively, are two smaller plates, each with a single bristle. There is therefore a transverse series of six prescutal bristles on each abdominal segment one to eight. The scutum is provided with a rounded, single bristle-carrying plate at each side of the middle line, thus giving a transverse series of two scutal bristles. The scutellum is the largest of the segment divisions, and bears dorsally a fused plate with two bristles extending equally to each side of the median dorsal line, similar to that on the prescutum. Lateral to this plate at each side is a smaller one with a single bristle. Ventral to this is the alar area, which has a fairly large plate, carrying posteriorly a long, and anteriorly a short bristle. The latter may belong to the scutal series, its supporting plate having fused with that on the alar region. Immediately ventral to the alar plate is the small, triangular, spiracular plate devoid of bristles; and further in the ventral direction is the epipleural plate, which occurs on the epipleural lobe—usually prominent, especially in young specimens. The epipleural plate is armed with three bristles: a long one posteriorly, and in the transverse row with posterior alar and scutellar bristles; a shorter one ventro-anteriorly; and a minute one dorso-anteriorly just below the spiracle. Ventral to the epipleural lobe are the coxal or hypopleural bristles—a long one posteriorly, and a short one anteriorly. The sternum is divided into two areas by a transverse fold. The anterior part is the presternum, and is not provided with any bristles or plates. The posterior area is the larger, and consists of the sternellum and post-sternellum. A large plate with two bristles occurs medianly on the sternellar area; and two smaller plates, which in older specimens are sometimes fused, are present on the post-sternellum. Each of the post-sternellar plates has a minute bristle medianly, and a much longer one laterally. On the post-sternellar plates of the eighth segment both pairs of bristles are minute.

The ninth abdominal segment forms the posterior extremity of the body. Dorsally it appears somewhat pear-shaped; and the tergum shows a granulated structure under a high power. It is armed with many bristles; but definite plates are not distinguishable, except a large transverse one on the sternum, which supports four long strong bristles. The other plates have fused to form the chitinised tergum. Prescutal and scutal regions are indicated by a pair of long and a pair of short bristles dorsally. Alar and epipleural regions are represented by a lateral slightly raised area, which carries one long and two short bristles. Spiracles are absent. The posterior margin is armed with a further series of three pairs of bristles; and towards the median line, at the posterior extremity, are two small circular pits. Hooks are absent. The tenth segment forms the anal proleg, and is placed

entirely ventral to the ninth. Small and narrow, it projects ventrally and slightly posteriorly to assist in locomotion, for which it is capable of being protruded and retracted. The armature consists of a transverse series of eight minute bristles near the apical border, two being posterior and the others anterior. The anus opens on the apex as a hollow slit. Unless in the region of the bristle-bearing and other chitinised plates, the cuticle of the body throughout is soft, with the surface raised into numerous, rounded, evenly distributed, wart-like tubercles (Pl. XVII, fig. 22). These are most apparent at the junction of two segments, i.e., in the intersegmental areas.

(vi) *The Spiracles.*—There are eight pairs of abdominal spiracles, all similar in structure, and placed latero-ventrally to the alar lobes. The circular peritrene is chitinised and slightly larger on the thorax and eighth abdominal segments. Surface examination shows each spiracle as a round hole, surrounded by a yellow band of chitin. This hole leads into a cup-shaped vestibule, having a small opening at the bottom. This is succeeded by a short narrow tube, having unstrengthened walls, and provided at the base with a long and a shorter arm, which project therefrom. Below these arms is a constricted area, from which the trachea proper arises. This peculiar arrangement in the spiracle was observed by Sanderson (56), but not understood. Diebel (17) and Böving (6) have since worked out the anatomy and mechanism of similarly constructed spiracles in other Chrysomelid larvae, and have shown that the two conspicuous arms which Sanderson considered as tracheal appendages belong to the spiracle, and, being provided with muscles, serve as regulators of the air-supply to the trachea. The writer has not yet had an opportunity of studying the internal anatomy of the spiracle in the larva of *L. parvulus*, but is satisfied that it is an essentially similar organ to that described for the other Chrysomelid larvae referred to above.

(vii) *Specific description of the bristles.*—In 1901 Sanderson (56) proposed a system whereby each bristle-carrying area received a number. Woods (64) followed Sanderson's idea, with modifications and additions in specific descriptions of species. The present writer has not adopted either, realizing that both are imperfect, and that it still remains for some worker on the larvae of many genera of Chrysomelidae to evolve a satisfactory scheme to include all possible variations. For example, both systems referred to provide only for larvae whose segments carry two transverse rows of bristles, whereas the larva of *L. parvulus* has three such rows, as already described. Moreover, a reference to a particular area or bristle by means of a number alone is both ineffective and cumbersome, and the system of MacGillivray (47), whereby bristles are referred to with respect to the particular area of the

segment from which they arise, is, in the opinion of the writer, more expressive.

MacGillivray's terminology is omitted here, and terms which have become general in descriptions of Coleopterous larvae substituted. Thus, the anterior tergal setae of MacGillivray are here prescutal ; posterior tergal, scutellar, etc. If it is desired to specify individual bristles in detailed descriptions, it is suggested that a system of numbering in conjunction with the naming of groups according to the position they occupy be adopted. Thus prescutal I. would refer to the bristle on the prescutum nearest the dorso-median line ; prescutal II. the bristle next lateral to No. 1, and so on. With such a system, the definite position of any individual bristle would at once be indicated.

(viii) *The "Prepupa"* (Pl. XVII, fig. 24).—Prior to pupation the fully fed larva undergoes certain changes whereby the shape materially alters. The body shrinks in strength while the diameter increases ; and, although the new form is of a different shape, it is still essentially the last instar, as no moult occurs during the shortening process. The length is now from 2·5 to 2·8 mm., with an average diameter of 1·8 mm. The form is cylindrical, and the position usually occupied is with the head and thorax curved strongly ventralwards, thereby giving a characteristic shape (Pl. XVII, fig. 24). By reason of the developing pupal structures underneath, the outline in the thoracic region is continually changing, and when nearing the last moult the thoracic sternites are pushed out into large protrusions for the accommodation of the developing legs, wings, elytra, etc., of the pupa. These structures can often be seen in suitably prepared specimens, and the one figured shows the small pads of the elytra as they appeared at that stage. The cuticle of the abdomen is now tough, and the outline of the segments well defined ; the intersegmental spaces appear in cleared preparations as areas traversed by lines or folds, but still show the wart-like tubercles. Many of the bristle-bearing plates are not now separately distinct, but would appear to have become approximated.

(*c*) *The newly hatched Larva* (Pl. XVI, fig. 9).—This is elongate in form, 0·7 mm. long and 0·16 mm. broad (average of six specimens). Body light yellow in colour, with head and posterior end of abdomen dark-grey to black. Three pairs of legs well developed, also anal-proleg. Just after hatching the cuticle is nearly transparent, and the digestive system shows through ; the tracheal system is now seen as fine silvery lines. The eight pairs of abdominal and one pair of thoracic spiracles are fully developed and functional. The head is comparatively large, and measures 0·15 mm. across the epicranial region. It carries the same number of bristles, and shows a similar arrangement of punctures as described for the head of the oldest

larva. The antennae are conspicuous, and the mouth-parts not different from those occurring in older larvae. The prothorax and pronotal shield are large, the latter not well chitinised, and with a distinct suture along the mid-dorsal line. It carries the normal number of bristles. The different plates of the mesothorax and metathorax are distinct; the two minute anterior alar bristles are not discernible; otherwise the arrangement is similar to that obtaining in old larvae. Epipleural lobes of abdomen not prominent; body cuticle, generally soft in the first eight segments of the abdomen, and bristle-plates indistinct. Normal number of bristles dorsally in prescutal, scutal, and scutellar series. The minute anterior alar bristle missing, and also the anterior-dorsal pleural bristle. Ninth abdominal segment large and well chitinised, and carries the normal number of bristles; they are larger than those on the other segments, especially the posterior ventral pair; these project conspicuously, and have their tips curved inwards.

(*d*) *Second-stage Larva* (Pl. XVI, figs. 10 and 11).—Length, 2·0 to 3·0 mm. Form very narrowly elongate, with the epipleural lobes projecting very conspicuously. Head, 0·19 mm. broad across epicranium. Segments of abdomen with well-defined prescutum, scutum, and scutellum. Arrangement of bristles as in final-stage larva. Bristle-plates distinct before the moult, and distantly separated owing to the expansion of the cuticle during growth. Ninth abdominal segment-bristles not longer than those on the other segments. Anal-proleg long.

(*e*) *The Pupa* (Pl. XIX).—Average length, 1·4 mm.; colour, creamy white; cuticle soft throughout, and easily crushed. The general form is short and stout, with the knees of the hind-legs projecting conspicuously at the sides, as is common in flea-beetle pupae generally. The head is bent underneath the thorax, by which it is obscured from dorsal view, while the posterior part of the abdomen is also bent ventralwards, and carries a pair of prominent curved and chitinised hooks. The developing mouth-parts are seen in week-old specimens. Antennae folded around the dorsal surfaces of the first and second pairs of legs quite near the knee-joints, and extend posteriorly and medianly to form graceful loops; their sheaths are provided with many prominent blunt processes, a circular series being present on the portion corresponding to each segment of the antenna. In young pupae the eyes of the developing adult are not distinct, but in older specimens they appear as large, dark-coloured areas, and a strong bristle arises from the pupal cuticle just above each. Besides these, the head is provided with another pair of strong bristles on the cranial region, which are supported on elevations of the pupal cuticle, while a further pair of smaller bristles occurs on the frons region. When viewed from the dorsal surface, the prothorax appears rounded

anteriorly at the vertex, from which there arise on rounded prominences two long bristles. Posteriorly, and towards the median line, are two smaller bristles, while posterior to these are two bristles of similar size to those on the vertex. A further pair arises near the lateral posterior angle, just in front of the mesothorax, and slightly dorsal and latero-ventrally at each side is another bristle. All these bristles are supported by pap-like elevations of the cuticle. The mesothorax is narrow, and carries four long bristles on similar prominences. Its posterior margin is modified to form a slight point at the median line, which projects posteriorly. This indicates the triangular scutellum of the adult. The pupal cuticle is continuous over the mesotergum and elytra, but underneath can be seen the sutures which mark the junction. The metatergum is much broader than the mesotergum, and has the scutellar groove distinctly shown as a longitudinal depression along the median line. At each side of this groove there are two bristles, thus making a transverse series of four. From the lateral angles of the metatergum the wings extend backwards around the sides of the body towards the median line on the ventral surface. The elytra extend similarly from the mesotergum, but the wings, being longer than the elytra, project well beyond the extremities of the latter. Just prior to emergence, the fine puncturing of the elytra is well seen through the pupal cuticle in suitably prepared specimens.

The legs are folded on the ventral surface, as shown in Pl. XIX, fig. 38. The front pairs are situate well forward, and are folded more or less transversely, while the hind ones are directed backwards to project at the sides of the posterior region of the abdomen. Each leg has near the knee a long and a short bristle dorsally, and a single short bristle ventrally. There are ten abdominal segments, nine of which are seen in dorsal view. Segments one to six are very much alike, and of about equal thickness. As the body tapers posteriorly, the sixth is much the narrowest transversely; the greatest breadth is attained by the second and third. Each of these segments has near the posterior margin of the tergites a transverse row of strong bristles or spines, which are supported on rounded prominences in the cuticle. Each row consists of four pairs—two pairs being dorsal, one pair lateral, and the fourth pair pleural and ventral to the spiracles.

The seventh abdominal tergite is large, and is produced posteriorly to form a rounded margin, which carries a transverse row of six long and two minute spines. The eighth tergite when viewed dorsally is small, and only projects slightly posterior to the seventh. It carries a similar transverse row of bristles. The ninth tergite is prolonged into two strong, inwardly curved, chitinised hooks, which resemble somewhat the forceps in the Forficulidae. These conspicuous structures serve definite purposes, which will be referred

to later. This segment carries at each side of the median line one long and three short bristles dorsally, two long bristles laterally, while two further bristles project between the anal hooks (Pl. XIX, fig. 42).

The tenth segment is very small, and is situated ventrally to the ninth, by which it is completely obscured in dorsal view.

The spiracles open in the pleural region of the metathorax and abdominal segments one to five; no spiracles can be seen on abdominal segments six to ten. A very short bristle occurs to the inner side of each spiracular opening, and similar bristles are present and occupy corresponding positions on the segments devoid of spiracles. The abdominal sternites are not armed, and as the pupa normally lies on its back in the cocoon, the projecting spines of the tergites serve to support the body, and prevent the possibility of damage from excessive moisture.

Unlike the pupae of some other Chrysomelidae, the males and females of this species do not differ in size. The chief external difference in the sexes is seen in the region of the two posterior abdominal segments. In the female these have, projecting from the ventral surface, two fleshy, finger-like structures, one at each side of the median line, and just anterior to the minute tenth segment (Pl. XIX, figs. 41 and 45). They serve to accommodate the palps of the ovipositor; and these organs can be seen during the later days of pupal life protruding into their pouch-like sheaths in suitably cleared specimens. In the male pupae no such projections exist; instead there is a single median enlargement, which presumably accommodates the aedeagus of the adult (Pl. XIX, figs. 43 and 44).

11.—Details of the Life-history.

In common with the other species of flea-beetles whose life-histories have been studied, *Longitarsus parvulus* spends the winter in hibernation in the adult state. Observations in Co. Derry go to show that the beetles issue from their winter quarters in spring, as soon as the weather becomes favourable—usually some time in April—and go in search of food prior to the commencement of reproductive activities. Early in May they migrate to fields of flax seedlings, and the females deposit their eggs in the soil from the middle of May onwards, according to the prevailing weather. Egg-laying may continue for about six weeks. In 1921 larvae were found from the 1st of June until late July, and pupae from the end of June until the middle of August. Emergence of the adults continued during the last weeks of July and throughout the first weeks of August. The maximum emergence of adults in 1920 was during the last week of August and the first days of September, but in 1921 a maximum was reached about the 25th July.

Prior to the emergence of these adults, and from the last week of June, few beetles are seen, because most of the old overwintering brood die before July, none having been found in the field after the middle of July, 1921. The newly emerged beetles feed for some time before going into hibernation, but they do not pair, nor do the females lay eggs; hence the species produces only one extended brood annually. If, however, the adults are caged throughout the winter on flax growing in a heated house, a brood will emerge early in May, as shown by an experiment conducted during the winter of 1920–21.

(*a*) *Pairing of the Adults.*—Actual pairing has not yet been observed, although a careful search was made from the 1st of May onwards. It is probable that general copulation had been effected prior to that date; and the fact that egg-laying commenced early in May would point to such having occurred. The warm weather which prevailed during late April of 1921 would, no doubt, influence early emergence from hibernation, and, simultaneously, early mating. Adults of *Chrysomela staphylea* and *Bembidium* sp. were observed in copulation as early as the first week of April. It is hoped to make earlier search for copulating adults next season, and in the winter quarters as well as on flax seedlings. As already indicated, no instance of mating such as that reported among some species of Chrysomelidae (38) has been observed in the newly emerged beetles prior to hibernation.

(*b*) *Oviposition.*—During the first week of May, 1921, several beetles were seen to be noticeably stouter in the abdominal region, and when such individuals were dissected, many light-yellow and nearly mature eggs were found in the ovarian tubes. These, then, are the gravid females, and as such can easily be distinguished from the smaller-bodied and more agile males. Eggs were first seen on the 16th May during the season of 1921 in one of the laboratory cages, and in the open field four days later. The latter had the appearance of having been deposited for some days, so that it is likely egg-laying commenced in the open about the 15th May, 1921. Observations on the life-history during the season 1920 were not commenced until July; but it is interesting to note that eggs were deposited by a caged female that season as late as the 10th July. No eggs were seen in the laboratory cages or in the open field after the 11th June, 1921, so that egg-laying may be said to have occupied about one month during season 1921, and to have extended from the first week in May to the first week in June, or roughly one month earlier than the single instance of egg-laying recorded in 1920.

Normally, the eggs are always deposited in the soil, but the actual position with reference to the flax plant does not appear to be important, as eggs have been found at different distances from the nearest plant. Eggs have

never been seen actually placed on the stem or roots in the open field, but in laboratory cages they have been found on the plant and on the roof of the cage, as well as in the soil. This only occurred where the cage was so small that the plant came in contact with the roof. The eggs are deposited in clusters of three, four, five, or more; but clusters of four appear to be most prevalent. Those in a cluster are firmly pressed side by side, and are often attached to a small lump of earth by means of a sticky substance at the ends.

A gravid female about to lay eggs descends from the feeding position on the plant by means of the stem to the soil. In this she chooses a suitable place in which to deposit a cluster of eggs, and this is usually somewhere near the plant, in fine soil, and covered with a few small lumps of soil, which serve as protection to the eggs. Therefore eggs are deposited in clusters just below the surface of the soil, and in close proximity to a flax plant. It cannot yet be definitely stated if oviposition occurs in flax-growing districts in soil other than that in which flax seedlings are growing. Beyond the fact that eggs were obtained over a period of one month, few data are as yet available regarding the length of individual oviposition periods, or the number of eggs deposited by each female. One female in captivity deposited thirty-seven eggs in fourteen days, but then escaped.

(*c*) *Period of Incubation.*—This, under the conditions which prevailed in the field laboratory, which differed little from those in the open, extended from fifteen to eighteen days. A record of the eggs deposited from the 16th May until the 10th June gave incubation periods extending as above, the mean of ten batches being 16·6 days.

(*d*) *Hatching.*—A short time before the incubation period is complete there is often seen a clear space towards one end of the egg, and at the same time the outline of the larva can be traced, the head being particularly distinct. From the nature of the rupture in the shell and its position, it is believed that the larva when ready for emergence uses the mandibles in the process of making the aperture through which it ultimately makes its exit. This becomes more apparent when egg-shells from which larvae have hatched are examined. Each has a similarly shaped aperture in a similar position, and corresponding to that occupied by the larval head before emergence (Pl. XV, fig. 8). It is supposed that a rounded area is first gnawed by the mandibles, and the rupture then completed by pressure of the thorax against that area.

(*e*) *Habits of newly hatched Larvae.*—These minute larvae are comparatively active, and are capable of crawling considerable distances. When hatched on blotting paper in the presence of flax roots, they crawled about slowly for some time, and ultimately went to a young portion of the root to

commence feeding. At this stage they are exceedingly fragile creatures, and highly susceptible to excessive moisture. The greatest difficulty was experienced in rearing them through to the second instar, and consequently few data regarding the first larval instar have yet been secured. Moreover, the feeding habit in the roots renders observation difficult. Individuals were seen to have moulted eight and nine days after hatching; but it cannot be said with certainty if this is the average length of the first stage. The larva becomes elongate as it grows older, but changes little in colour. Before the moult it is narrowly elongate, and the bristle plates are well seen in cleared specimens, while the head, and also the posterior extremity, appear as yellow chitinised areas.

(*f*) *Second Instar: Duration and Habits.*—The actual moulting process has not been observed; but from the study of the larva just before the moult, it is inferred that the old cuticle splits along the mid-dorsal line of the thorax, the rupture occurring in the sutures of the dorsal plates of the three thoracic segments, and continuing towards the anterior of the head by way of the epicranial and frontal sutures. Moulting is known to occur in the leaf-tunnelling larvae of *Phyllotreta nemorum* inside the tunnel; and it is believed that in the case of *L. parvulus* moulting usually occurs while the larva is still feeding in the tunnel of the root. The larva is now longer and a little stouter, and is thus admirably adapted for the habit which it possesses of burrowing into the younger roots and feeding on their soft parenchymatous tissues. Entrance is secured by means of a round hole not much larger than will admit the larva. From this hole the tunnel usually extends downwards into the younger and softer parts of the root. The larvae occasionally come out of the tunnels to enter the root again at some other part.

The length of the second larval stage was not determined by actual observation, but from the appearance of the bristle plates, and from measurements of the head, it is thought the instar has a somewhat similar duration to that of the first.

(*g*) *Final Instar: Duration and Habits.*—Feeding in the root continues for a week or more after the second moult, and the habits continue the same. When fully fed, the larva leaves the root and comes into the soil. There it wanders about, and ultimately prepares a crude cocoon of soil in which it becomes transformed by a process of shrinkage in length, accompanied by an increase in thickness, to what American workers term the "prepupa." It is simply the final instar modified into a particular form during the transition from active feeding larval life to the quiescent pupal condition.

The total larval life from the time of hatching until the "prepupa" is

formed lasts from twenty-three to twenty-eight days. An elongated and fully fed larva becomes transformed rapidly to the shortened quiescent condition; and usually on the second day after the cocoon has been completed the short and stout form is assumed. This condition persists for five or six days, during which the larva remains in a passive condition and exhibits little movement.

When the development of the pupal structures is complete, the larval cuticle splits open along the median line of the thorax, and along the epicranial and frontal sutures of the head, and the pupa emerges in the cocoon. The old cuticle is thrown off backwards, and is rarely seen attached to the pupa.

It is interesting to note here that the larvae of all the other species of *Longitarsus* studied, so far as the writer is aware, possess similar feeding habits by living in and feeding on the roots and stems of the adult's host plant. Thus the larvae of *L. echii* Koch. feed beneath the root-bark of *Echium vulgare* (53); *Longitarsus niger* Koch. larvae also penetrate and feed upon the roots of this plant. The larvae of *Longitarsus tabidus* F. live in the root-tissues of *Verbascum* spp. (54); while the larvae of *Longitarsus luridus* Scop. live in the stems of *Rhinanthus* sp. near the ground-level (55).

(*h*) *Duration and Characteristics of the Pupa.*—The pupa remains quiescent in the cocoon, but is capable, if disturbed, of making considerable movement by lashing the hinder region in circular motion. This movement occurs as the pupa lies on its back, and is permitted by the articulation of the abdomen with the thorax. When movement in the head region is desired, the anal forceps are pressed firmly against the wall of the cocoon, and when a hold is secured, the head is moved as desired. Thus the anal hooks serve to anchor the pupa in the cocoon, and they also aid considerably in the casting of the pupal cuticle. Pupae formed during the period extending from the 1st till the 25th July were kept in soil, and the adults emerged from the 14th July until the 8th August. The pupal stage therefore extends from ten to fifteen days, with an average duration of twelve days. The pupal cocoons are formed from $1\frac{1}{2}$ to $2\frac{1}{2}$ inches below the surface of the soil.

Colour-changes in the Pupa.—When first formed the pupa is creamy white throughout, and shows no trace of pigment in the eyes. After three or four days pigment appears, and the eyes of the imago are seen as brown patches, while the rest of the pupa is still white. As development proceeds, the colour changes in many parts, so that just before the emergence of the adult the pupa has become dirty white, while the eyes appear as dark-brown to black areas occupying a considerable portion of the head region; the tips of the mandibles are orange-yellow; the femora pale-yellow, with a deeper

yellow region in their centres; and the anal hooks yellowish-brown at the tips. The development of pigment in the eyes offers a useful means for determining the age of individual pupae.

(*i*) *Characteristics of the newly emerged Adult.*—Colour, white or greyish white, with greyish black head, black eyes, and yellow femora. After three days it is greyish black all over; and after a further three days the normal colour has been assumed. Newly emerged beetles can therefore be easily recognized in late summer when they appear above ground. They are not, however, seen until the colour has become dark-grey or brown, as they remain in the soil for the first few days of adult life. Just after emergence they can jump tolerably well, but they walk with difficulty.

(*j*) *Duration of the Life-cycle.*—The transformations from oviposition to the emergence of the adult are thus completed in from fifty-seven to sixty-five days.

The figures in the following table are taken from records of rearing experiments :—

Eggs deposited.	Hatched.	Incubation period.	Fully fed larva in soil.	Feeding larval stage.	Pupa formed.	Length of non-feeding larval stage.	Adult emerged.	Length of pupa stage.	Total from egg to adult.
		Days		Days		Days		Days	Days
16.5.21	2.6.21	17	25.6.21	23	1.7.21	5	12.7.21	12	57
19.5.21	4.6.21	16	1.7.21	27	8.7.21	6	20.7.21	12	61
23.5.21	9.6.21	17	7.7.21	27	13.7.21	6	25.7.21	12	62
26.5.21	11.6.21	16	10.7.21	28	16.7.21	6	29.7.21	13	63

(*k*) *Hibernation of the Adults.*—As soon as the weather gets cold, feeding ceases, and winter quarters are secured. Hibernation occurs beneath the shelter of grass, weeds, moss, &c., near dry fences in the neighbourhood of the fields which supported them during the previous weeks. Hibernating beetles are also found in crevices in walls, gate-piers, woodwork, &c.; in outhouses, adjacent to flax fields, and even far out in fields from which flax has been pulled, if these are provided with old grass and weeds to afford shelter. In January, 1921, the writer made a study of the hibernating quarters, and found beetles in the different places as stated. Some go down into the soil for a short distance, while others are found in crevices and cracks in the soil, or even on the surface beneath grass, &c. When first seen they are quite inactive, with the legs gathered underneath the body, and the

antennae folded by the sides. They lie in the normal position. On the application of slight heat, or when disturbed, slow movement begins; and after the legs and antennae have assumed the normal positions, a beetle may commence to walk or even jump away from the place of hibernation. Even then, however, they are sluggish in movement and readily reassume a quiescent state.

Hibernation usually occurs in October, or in late September, if the weather is severe. In early October, 1920, the beetles were observed going into hibernation, although individuals were seen on the 19th of October feeding on flax seedlings which were growing in the dug portion of a potato field from seed spilled there.

12.—Natural Checks and Enemies.

Various birds were seen to prey on the larvae and pupae when exposed to their view. Some adults become entangled in the webs of spiders placed near the soil, and thus fall a prey to them. A carabid beetle, *Bembidium lampros* (which Mr. Halbert kindly identified), was seen early in May to attack the gravid females; and by placing three of the latter in a tube containing some small lumps of soil with two of the carabids, it was found that by next day two of the flea-beetles had been devoured.

It is highly probable that *B. lampros* is also predaceous on the eggs, although this has never been actually observed. This species of ground beetle was exceedingly abundant in the soil of the experimental plots throughout the 1921 season.

Larval mites of the family Trombidiidae have been found attached to the adults. One specimen which Mr. Halbert believes to be the larval form of *Rhyncholophus phalangeoides* was attached to the abdominal tergites underneath the right elytron. Many mites belonging to the family Tyroglyphidae have been found attacking larvae and pupae in rearing cages; but their presence was probably accidental, and they cannot be regarded as natural enemies in free life.

The larvae and pupae appear to be singularly free from the attacks of Hymenopterous parasites. Not a single internal parasite has been reared from the hundreds of larvae and pupae collected outside and brought through to the imago in the laboratory. This would appear to be the general condition in the flea-beetle group.

13.—Suggestions for Control Measures.

It is an acknowledged fact that weak, slow-growing seedlings in thin brairds are, for some unknown reason, particularly liable to attack, and,

because they are less capable of outgrowing and overcoming the attack, suffer more than those in strong, vigorous brairds. It follows, therefore, that anything which tends to encourage the strong, vigorous growth of the seedlings is, indirectly, a preventive measure against the chances of extensive damage. Hence the importance of using only seed of first-class germinating capacity, and of sowing it only on suitably prepared and properly manured fields.

As already suggested, the time of sowing may have a considerable influence on the intensity of an attack; and, as the earlier brairds often suffer considerably, while those appearing later practically escape, it is evident that very early sowing is not desirable in districts where the flax flea-beetle is prevalent. It is certainly not desirable to sow isolated fields early, but rather should it be the aim to get all the flax in a particular district sown at approximately the same time, as the beetles, when spread over a considerable area, are less liable to cause serious damage in any particular field.

The sowing of small areas of flax at least one week earlier than the main part of the crop, and using these areas as traps on which to catch beetles attracted thereto, suggests itself as a method whereby large numbers may be destroyed. The destruction of the beetles is best achieved by sweeping over the seedlings a sack or light board, coated with tanglefoot or other sticky material, in which the disturbed beetles are caught and held. Such operations give best results when done during bright sunlight (when the beetles jump most readily from the food plants), and in such a manner as to facilitate their jumping against the sticky board when disturbed. The sweeper should be regularly cleaned, and fresh coats of the sticky material applied. As the beetles appear to be attracted to white-coloured areas, the sweeper should be as white as possible, and, even when left lying in the vicinity where beetles abound, these sweeping boards may trap considerable numbers.

Further destruction may be effected by the thorough cultivation of the trap plots in late June, which kills any eggs laid during May and early June, and any larvae newly hatched therefrom.

Excellent results have been obtained from the use on attacked seedlings of light dressings of stimulating manures before the attack has extensively developed. Thus, a dressing of not more than ½ cwt. of nitrate of soda per statute acre has been found highly beneficial when applied to attacked brairds.

Trials of various possible remedies were made at Coleraine during the season 1921. These consisted of dressings of the seed, and dusts and sprays applied to the seedlings. Some of the latter were intended to act as repellents by creating a noxious smell, or otherwise making the seedlings distasteful to the beetles; others were intended to act as poisons; while a few were

expected to have both these properties. Most of the experiments gave indefinite information owing to the unusually slight infestation. There were, however, indications that a few possessed effective properties; but many further tests are necessary before they, or modifications thereof, can be recommended. The very evident uselessness of other treatments tested pointed to the conclusion that further trials with such would be superfluous.

With the object of determining the effect, if any, of various seed dressings, some of which were reputed to impart protective properties, small plots were sown with seed previously treated as follows :—

1. No dressing (control).
2. "Nilfli" powder, mixed dry with the seed.
3. Powdered naphthalene, mixed dry with the seed.
4. Two per cent. copper sulphate solution.
5. Two per cent. copper sulphate solution, plus paraffin oil.
6. Paraffin alone.

The powders were mixed at the rate of 21 lbs. to 7 pecks of seed, while the liquids were sprayed on during continual stirring, and until the seed became thoroughly wetted. Slaked lime was used as a drying agent, and sowing done directly afterwards. The germination was not adversely affected by any of the treatments employed, but in no case was the slightest protection afforded to the seedlings. All six plots were equally badly attacked, and no difference could be seen in the severity of the attack on the control plot when compared with each of the others.

The following substances were applied in powder form to the seedlings, and as far as possible in the presence of dew, to ensure better adhesion to the foliage :—

1. Flowers of sulphur, 1 cwt. per acre.
2. Corry's tobacco powder, 1 cwt. per acre.
3. Pyrethrum powder, 1 cwt. per acre.
4. Soot, 6 cwt. per acre.
5. Soot and lime, equal parts, 6 cwt. per acre.
6. Road dust, 6 cwt. per acre.

Negative results were obtained from each of these powders, no obvious protection being afforded the seedlings in any of the plots so treated.

The glabrous nature of flax foliage is responsible for a serious difficulty with regard to sprays for the seedlings. Moreover, the habit possessed by the beetles of feeding only on the newly opened foliage renders the effective

destruction of the insects with a poison wash sprayed on the seedlings more remote, since new foliage untouched by the poison wash is rapidly produced. Therefore, when considering likely useful washes, the possibility of improving the adhesive properties of well-known poisonous substances by the addition of agents reputed to impart such properties was primarily considered, as was also the possibility of combining a wash which, as well as being poisonous, had a deterrent effect. Different strengths of Bordeaux mixture were used alone, and also with the addition of (*a*) casein, (*b*) flour paste, and (*c*) soft soap, to test the comparative adhesive and spreading properties of the resulting mixtures. These properties were not, however, observed to be appreciably increased by any of these substances. Bordeaux mixtures, with the addition of (*a*) lead arsenate, (*b*) 98 per cent. nicotine, (*c*) lead arsenate and flour paste, and (*d*) lead arsenate and soft soap, were also tried. The last-named mixture scorched the seedlings, but not beyond recovery. In all the other cases no appreciable damage to the seedlings could be detected. Other washes used were lead arsenate, lead arsenate-paraffin emulsion, potassium chromate, potassium sulphide, Burgundy mixture, and copper sulphate solution alone.

Lead arsenate spreads and adheres very indifferently to flax seedlings, while lead arsenate-paraffin emulsion would appear to be little better; moreover, the latter scorched and browned the seedlings to a considerable extent. Both potassium sulphide and chromate are poor spreaders, and adhere badly, so that they are unsuitable for use alone on flax. The former was intended to neutralize the supposedly attractive stimulus emitted by the brairding seedlings, but it did not appear to possess that property.

The slight infestation of beetles during the season is to be regretted from the point of view of testing possible remedies, and little can be said regarding the usefulness or otherwise of many of the washes used. Bordeaux mixture, however, gave indications of acting as a deterrent to the influx of beetles on plots to which it was applied alone, or in conjunction with lead arsenate or nicotine.

A Bordeaux mixture containing about 1½ per cent. of free copper sulphate was also tested, and this, besides having the deterrent properties of the others, had the effect of destroying weeds such as Spurrey (*Spergula arvensis*) and Charlock (*Sinapis arvensis*), both of which were present to a considerable extent; the flax seedlings were not, however, injured. Next season it is hoped to continue experiments dealing with probable preventive and remedial measures.

Finally, it should always be borne in mind that to wage war on anything about the farm that is calculated to afford shelter for the beetles during the

winter is, indirectly, a preventive measure against future attacks. Hence all grass and weeds present on fields from which a crop of flax has recently been removed (besides that occurring on ditch-backs and dry banks beside or near such fields) should be destroyed or grazed bare by stock, for by so doing the beetles are deprived of many suitable places for hibernation, and are, consequently, exposed to greater risks during the winter months.

It is the writer's opinion that the practice of sowing grass seeds with the flax, common in some districts, facilitates the perpetuation of this pest, because such a practice provides for the needs of the beetles at critical periods. Thus, after the flax has been pulled and removed, they have ample suitable food in the young grasses and clovers, and, later, sufficient protection for hibernation is afforded practically anywhere in the field.

Thorough cultivation after the removal of the flax, besides removing food and hibernation quarters, is desirable from another aspect. If, as was the case in 1920, the brood of beetles has not emerged at the time of pulling the flax, many of the soft, delicate pupae in the soil will be destroyed or brought to the view of birds by such processes. These cleaning and cultivating operations are purely preventive measures; but now that more is known of the life of the pest, they at once suggest possibilities in the keeping down of numbers, and thus minimizing future attacks.

14.—Summary.

1. This paper deals with the flax flea-beetle (*Longitarsus parvulus* Payk.), a serious insect enemy of flax, and one responsible for considerable loss to growers of this crop in Ireland.

2. The history and synonymy, identity, distribution, and allied species are discussed. In Ireland the species is commonly found all over Ulster, and of recent years it has become a pest in flax-growing districts in Co. Cork.

3. The adult is a leaf-eater, and causes serious damage to brairds of flax seedlings. By eating the cotyledons and growing point many of the seedlings are killed outright, while others remain small and stunted, and many become branched.

4. Cultivated flax is the favoured food-plant of the adults, but they also eat clovers, grasses, and species of wild flax.

5. Past records of damage to flax are given, with a discussion on the conditions which probably favour attacks.

6. The life-history has been followed, and the immature stages are described and figured for the first time.

7. The adults hibernate in sheltered positions underneath grass, weeds, etc., and in cracks and crevices in the soil or in ditches and walls, during the winter, and come out in spring, when the weather becomes favourable.

8. The females lay eggs in the soil in which flax is growing from early May to late June. These hatch in sixteen days, giving rise to minute larvae, which bore into and feed on the roots of the flax plants, but do not appear to cause any appreciable hindrance to growth.

9. The feeding larval life occupies about twenty-seven days, during which time the larvae increase in size and become slenderly elongated in shape. When fully fed the larvae leave the root-tunnels and go into the soil, where they transform to pupae in crude cocoons of earth.

10. The pupa is small and stout, soft and white, and from it the adult emerges after twelve days. Emergence reached a maximum in Co. Derry about the 25th July, 1921, which was a month earlier than that observed the previous season.

11. The complete life cycle from egg to adult is passed in about sixty days, and there is only one generation annually.

12. The species is particularly free from the attacks of internal parasites, and no serious natural enemy has been observed.

13. Preventive measures consist of the production of strong, vigorous growing brairds by the employment of suitable cultivation, seed, and manure; and in the destruction or removal of all likely hibernation quarters, especially near fields which recently grew a flax crop. Early sowing of isolated fields should be avoided.

14. The stimulation of attacked seedlings by the application of a light dressing of nitrate of soda has proved beneficial.

15. Experiments carried out in Co. Derry during the 1921 season indicate the possibility of the use of Bordeaux mixture as a deterrent. Owing, however, to the very slight infestation that season, the information gained from trials on possible remedial sprays is not sufficient to warrant the recommendation of any particular treatment, and further trials are very necessary and desirable in this connexion.

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EXPLANATION OF PLATES.

PLATE XV.

Fig.

1. Photograph of flax seedlings, showing early effect of flea-beetle attack. (Natural size.)
2. Cotyledons of a seedling enlarged to show the holes and notches made by the beetles. (× 3.)
3. An enlarged photograph of a seedling, showing the central bud eaten. (× 3.)
4. Photograph of older seedlings, showing the general effect of an attack. (Natural size.)
5. Enlarged photograph of an older seedling after a severe attack. (× 3.)

PLATE XVI.

6. Eggs of *Longitarsus parvulus*. (× 75.) *ps*, pad of sticky substance often present at the end.
7. Portion of the egg-surface very highly magnified.
8. Egg after hatching. (× 85.) *ea*, emergence aperture of larva.
9. Newly hatched larva. (× 122.)
10. Second stage larva; dorsal view. (× 50.) *prs*, prescutum; *sc*, scutum; *scut*, scutellum.
11. Second stage larva; lateral view, with cuticle cleared. (× 50.)
12. Dorsal view of thorax of mature larva, showing the arrangement of the bristle-bearing plates. (× 70.) *su*, pronotal suture; *P*, prothorax; *Ms*, mesothorax; *Mt*, metathorax.
13. Ventral view of thorax and first abdominal segment of mature larva, showing the sternal plates. Legs removed. (× 70.) *P*, prothorax; *Ms*, mesothorax; *Mt*, metathorax; *A1*, first abdominal segment.
14. Plan of bristles and bristle-carrying plates of abdominal segments one to eight. Drawn from third abdominal segment. (× 70.) *MD*, mid-dorsal line; *MV*, mid-ventral line; *prs*, prescutal plates and bristles; *sc*, scutal plates and bristles; *scut*, scutellar plates and bristles; *al*, alar plate and bristles; *sp*, spiracular plate and spiracle; *ep*, epipleural plate and bristles; *hyp*, hypopleural plate and bristles; *st*, sternal plates and bristles.

Plate XVII.

Fig.

15. Dorsal view of posterior extremity of fully grown larva. (× 105.) *A8*, eighth abdominal segment; *A9*, ninth abdominal segment; *epl*, epipleural lobe and bristles; *scub*, scutellar bristles.
16. Lateral view of posterior extremity of fully grown larva. (× 105.) *A8*, *9*, *10*, abdominal segments 8, 9, and 10; *sp*, spiracle; *epl*, epipleural lobe.
17. Ventral view of posterior extremity of fully grown larva. (× 105.) *an*, anus; other lettering and figures as before.
18. Left mesothoracic leg of larva; inside view. (× 550.) *tu*, tunica; *cl*, claw; *ts*, tarsus; *tb*, tibia; *cx*, coxa; *fm*, femur; *tr*, trochanter; *ac*, acetabulum.
19. Right metathoracic leg of larva; outside view. (× 550.) Lettering as above.
20. Seventh abdominal spiracular plate and spiracle; surface view. (× 1,100.)
21. Seventh abdominal spiracle; lateral view. (× 1,100). *nk*, neck of spiracle; *aca*, arms of the closing apparatus; *tra*, trachea.
22. Portion of the larval cuticle very highly magnified.
23. Final-stage larva drawn from life. (× 38.)
24. "Prepupa" of final instar from life. (× 47.) *1–10*, abdominal segments; *wp*, outline of developing wing-pads of pupa; *al*, alar lobe of metathorax; *epl*, epipleural lobe of fifth abdominal segment; *prs*, prescutum; *sc*, scutum; *scut*, scutellum; *sp*, spiracle.

Plate XVIII.

25. Head of fully grown larva; ventral view. (× 200.) *an*, antenna; *ca*, cardo; *cl*, clypeus; *ep*, epipharynx; *epc*, epicranium; *gal*, galea; *gu*, gula; *hyp*, hypopharynx; *lbr*, labrum; *lig*, ligula; *lp*, labial palp; *me*, mentum; *mn*, mandible; *mp*, maxillary palp; *pfl*, labial palpifer; *pfm*, maxillary palpifer; *pr*, prothorax; *sm*, submentum; *st*, stipes.
26. Head of larva; dorsal view. (× 200.) *eps*, epistome; *epsu*, epicranial suture: *fr*, frons; *frr*, frontal ridge; *frs*, frontal suture; *upb*, ultraposterior punctures and bristles. Other lettering as in fig. 25.
27. Head of larva; lateral view. (× 200.) *pls*, pleurostome. Other lettering as in fig. 25.

Fig.

28. Right antenna of larva; dorsal view. (× 600.) *1*, *2*, *3*, segments; *spr*, sensory projections.
29. Right mandible; inside view. (× 600.) *abd*, abductor muscle; *add*, adductor muscle; *cd*, condyle.
30. Left mandible; inside view. (× 600.) Similar lettering.
31. Right maxilla; ventral view. (× 600.) *ca*, cardo; *gal*, galea; *lac*, lacinia; *mp*, maxillary palp; *pfm*, maxillary palpifer; *st*, stipes.
32. Hypopharynx and maxillae; inside view. (× 375.)
33. Left maxilla; inside view. (× 600.) *gal*, galea; *hyp*, hypopharynx; *lac*, lacinia; *mp*, maxillary palp; *pfm*, maxillary palpifer.
34. Labrum and clypeus; dorsal view. (× 520.) *cl*, clypeus; *pb*, punctures with minute bristles.
35. Clypeal punctures and bristles. (Very highly magnified.)
36. Epipharynx. (× 520.)
37. Labium; ventral view. (× 600.) *hyp*, tip of hypopharynx; *lig*, ligula; *lp*, labial palp; *pfl*, labial palpifer; *me*, mentum; *sm*, submentum.

PLATE XIX.

38. Female pupa; ventral view. (× 65.)
39. „ „ ; dorsal „ (× 65.)
40. „ „ ; lateral „ (× 65.)
41. Anal segments of female pupa; ventral view. (× 125.)
42. „ „ male „ ; dorsal „ (× 125.)
43. „ „ male „ ; lateral „ (× 125.
44. „ „ male „ ; ventral „ (× 125.
45. „ „ female „ ; lateral „ (× 125.)

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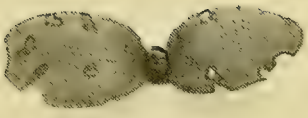

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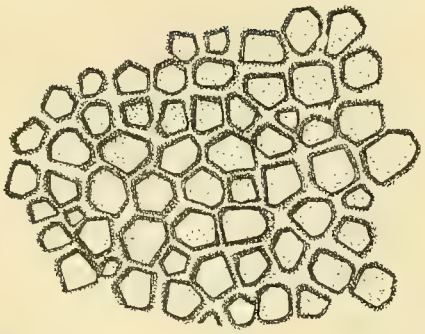

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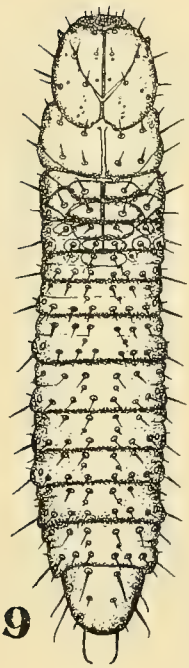

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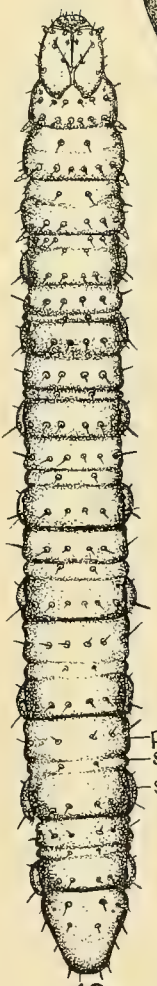

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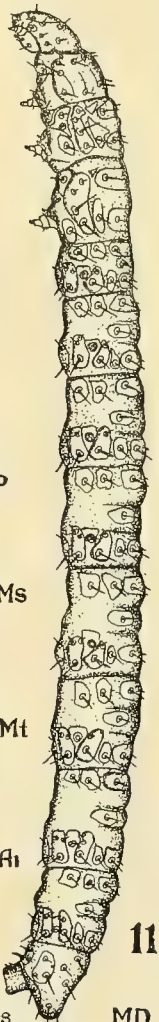

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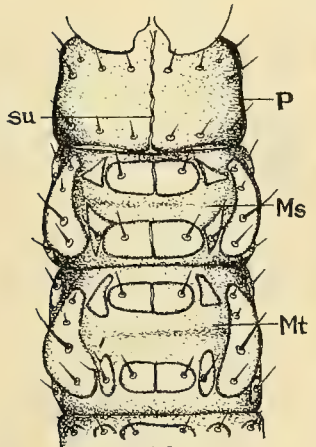

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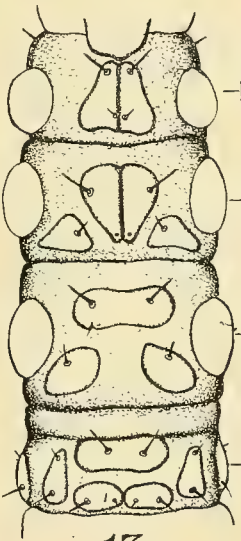

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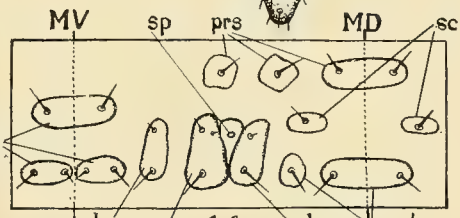

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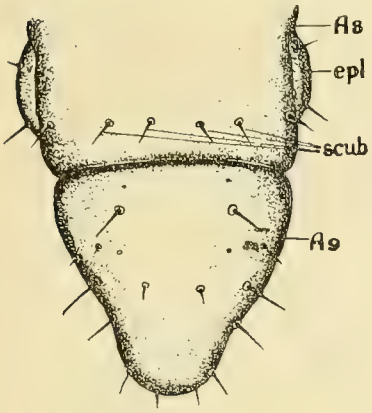

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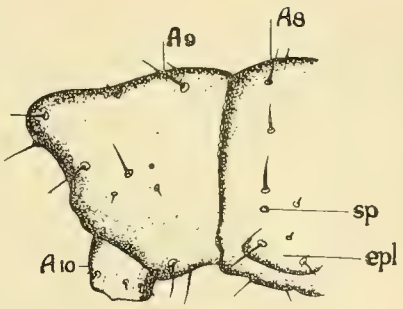

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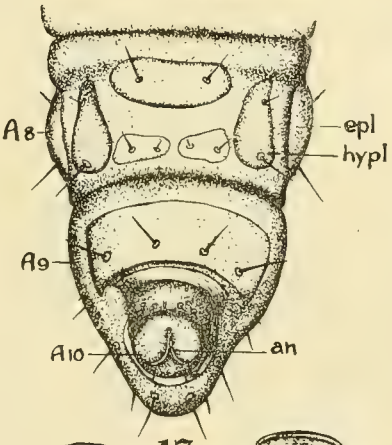

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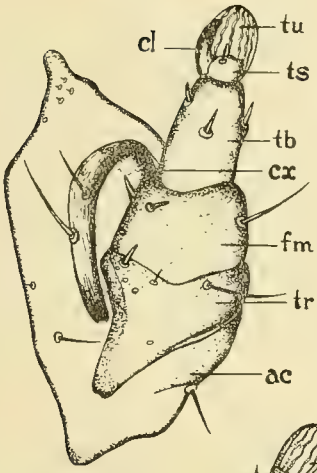

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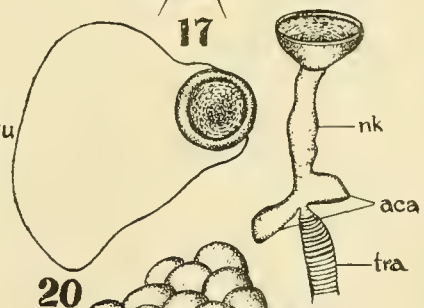

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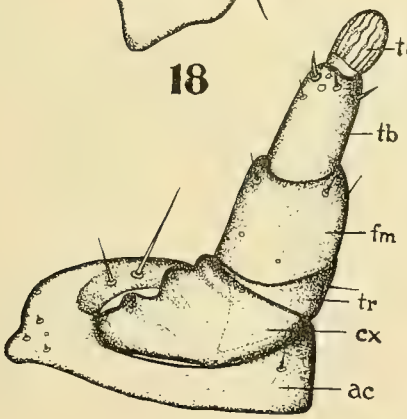

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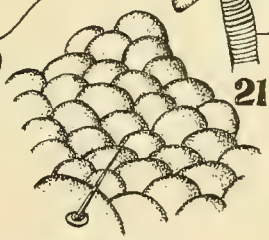

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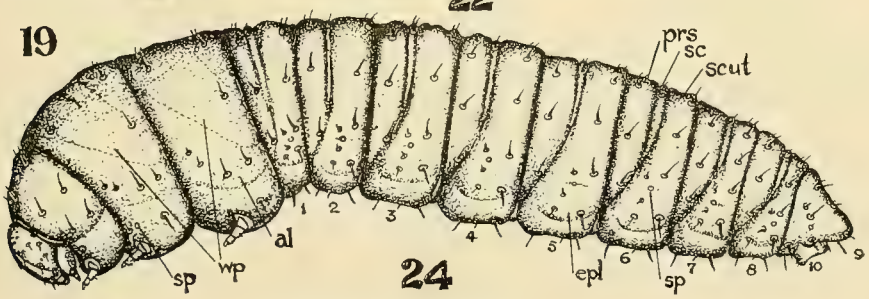

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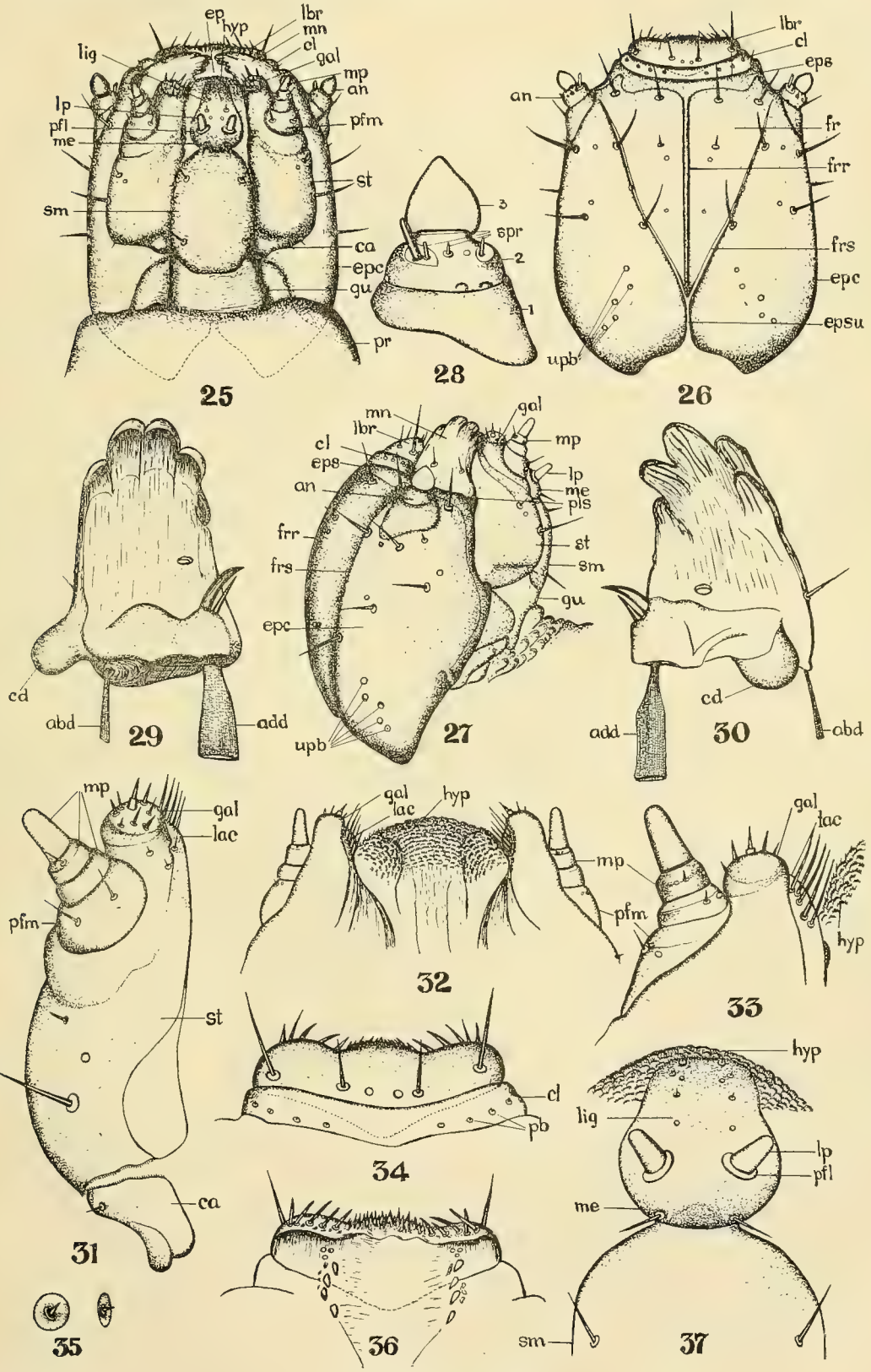

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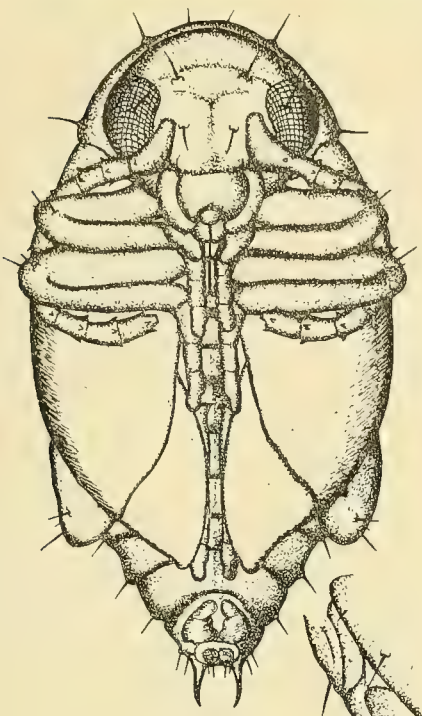

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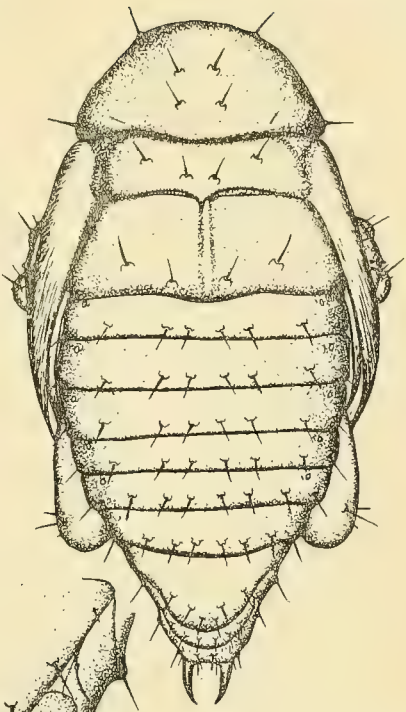

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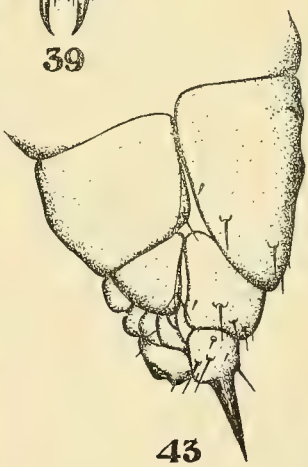

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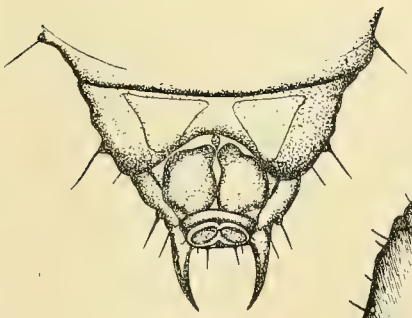

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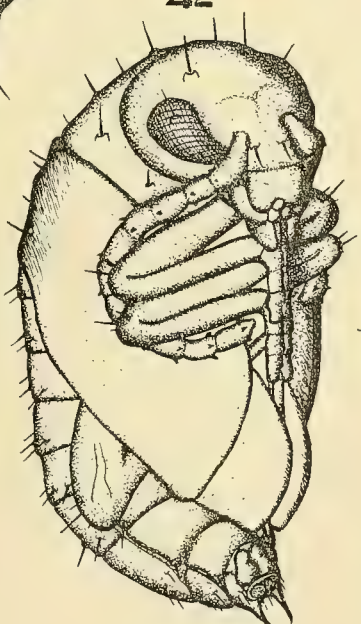

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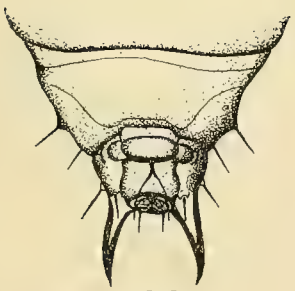

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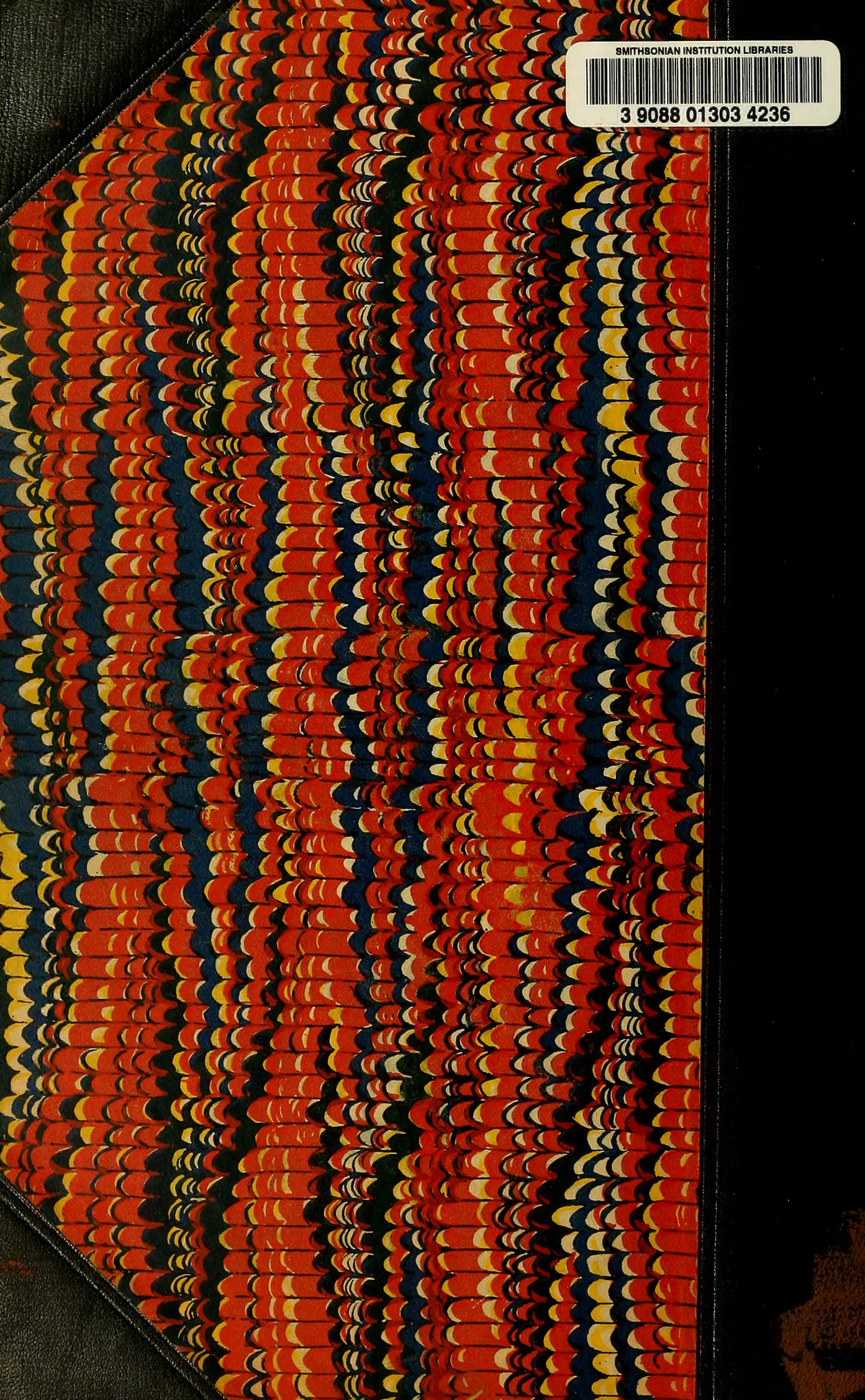
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